Preparation of Novel Reactive Plastisol Based on Poly(vinyl chloride) and Multifunctional Acryl Esters

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ABSTRACT: Poly(vinyl chloride) (PVC) powder was mixed with various polyfunctional acryl monomers as plasticizers to prepare acrylate-modified plastisols. This class of plastisol was hardened into the B stage without reaction and then cured into a harder material through crosslinking of the acrylate. The best formulation was attained after evaluation of various acrylates, PVC grades, and peroxides. Several difunctional acrylates with solubility parameters similar to that of PVC could be most conveniently used as the plasticizer. A sheet molding compound was obtained by the combination of the resultant plastisols with glass fiber by compression molding using conventional machines. It was cured into a PVC-based fiber reinforced plastic with high performance. This class of acrylate-modified plastisol is called reactive plastisol. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1794–1801, 2000

Key words: poly(vinyl chloride); acryl esters; plastisol; sheet molding compound; fiber reinforced plastic

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the common plastic resins used all over the world. Thus far, various methods have been devised and used for the processing of PVC. One of the practical methods that is often used is based on so-called plastisol, which is particularly efficient in coating, slush molding, and so forth.[1,2]

Plastisol is a paste composed of PVC fine particles and plasticizer (without solvent added). This paste solidifies by incorporation of the plasticizer in the PVC particles that is induced by heating to a certain temperature.[3,4] This nature allows easy coating and molding in which the paste is cast in a mold and simply cured by heating without evaporation of the solvent. However, the resulting plastic material is sometimes too soft and mechanically weak, because a relatively large amount of plasticizer is needed for making fluid plastisol. Furthermore, the plasticizer incorporated in the plastic material likely migrates to the surface area to induce unfavorable adhesion and morphology change. These drawbacks limit the range of application of plastisol.

This article discloses a new type of plastisol that is incorporated with polymerizable acryl monomers instead of ordinary plasticizers. Because the acrylates can work not only as plasticizers but also as radical crosslinkers, the acrylate-modified plastisol can be crosslinked into a harder material by the postcuring conducted after thermal hardening for solidification (the so-called B stage). This curing behavior allows us to make fiber reinforced plastics (FRPs) by the combination of the plastisol with glass fiber (chopped

Table I   Acrylates Used as Reactive Plasticizer

	Monomer	Abbreviation	Supplier
1	2-Hydroxyethyl 2-methyl-2-propenoate	HEMA	Nihon Shokubai
2	Oxiranylmethyl 2-methyl-2-propenoate	GMA	Nihon Shokubai
3	2-Ethylhexyl 2-propenoate	EHA	Nihon Shokubai
4	1-Ethenyl-2-pyrrolidinone	NVP	Nihon Shokubai
5	(Tetrahydro-2-furanyl)methyl 2-propenoate	THFA	Nihon Kayaku
6	3a,4,7,7a-Tetrahydro-4,7-methano-1H-indenyl 2-propenoate	DCPDA	Kyoeisya Kagaku
7	2,2-Dimethyl-1,3-propanediyl bis(2-propenoate)	NPDA	Toua Gousei
8	(1-Methyl-1,2-ethanediyl)poly[oxy(methyl-2,1-ethanediyl)]bis(2-propenoate)	PPA	Sanyo Chem. Ind.
9	2,2-Dimethyl-1,3-bis(2-methyl-2,1-thanediyl)bis(2-propenoate)	NPPA	Sanyo Chem. Ind.
10	4,8-Bis[(1-oxo-2-propenyl)-oxy]tricyclo[5,2,1,0²,⁶]decane	TCDA	Sanyo Chem. Ind.
11	(1-Methylethylidene)bis(4,1-cyclohexyleneoxy-2,1-ethanediyloxy-2,1-ethanediyl)bis(2-propenoate)	HBEA	Sanyo Chem. Ind.
12	(1-Methylethylidene)bis(4,1-cyclohexyleneoxy-2-methyl-2,1-ethanediyloxy-2-methyl-2,1-ethanediyl)bis(2-propenoate)	HBPA	Sanyo Chem. Ind.
13	(1-Methylethylidene)bis(4,1-phenyleneoxy-2,1-ethanediyloxy-2,1-ethanediyl)bis(2-propenoate)	BPEA	Sanyo Chem. Ind.
14	2-Ethyl-2-[[(1-oxo-2-propenyl)oxy]methyl]-1,3-propanediyl bis(2-propenoate)	TMPA	Toua Gousei
15	1-[[(1-Oxo-2-propenyl)oxy]-2,1-ethanediyloxy]-2,2-bis[[[(1-oxo-2-propenyl)oxy]-2,1-ethanediyloxy]methyl]-butane	TMPEA	Sanyo Chem. Ind.
16	1-[[(1-Oxo-2-propenyl)oxy]-2-methyl-2,1-ethanediyloxy]-2,2-bis[[[(1-oxo-2-propenyl)oxy]-2-methyl-2,1-ethanediyloxy]methyl]-butane	TMPPA	Sanyo Chem. Ind.
17	2,2-Bis[[(1-oxo-2-propenyl)oxy]methyl]-1,3-propanediyl bis(2-propenoate)	PETA	Sanyo Chem. Ind.
18	2-[[3-Hydroxy-2,2-bis[[(1-oxo-2-propenyl)oxy]methyl]propoxy]methyl-2-[[(1-amoxo-2-propenyl)oxy]methyl]-1,3-propanediyl]bis(2-propenoate)	DPHA	Sanyo Chem. Ind.

strand). Here we demonstrate such applications by making sheet molding compounds (SMCs) that are processed by compression molding using conventional machines. Based on these interesting characteristics of the acrylate-modified plastisol, we call it reactive plastisol.

EXPERIMENTAL

Materials

Samples of PVC, acrylates, and peroxides were purchased and used without purification. Their suppliers and abbreviated names are listed in Tables I–III. The solubility parameter of each acrylate was calculated by Fedor's equation.[5] The values are presented in Table IV.

Preparation of Plastisol

A basic formulation is as follows. A predetermined quantity of PVC powder was charged into a beaker and mixed with an acrylate and a peroxide. The weight ratio of the acrylate to PVC was 100/100 in parts, and the amount of the peroxide was 3–5 wt % relative to the weight of the acrylate; 2 wt % zinc stearate (Wako Chemical Co.,

Table I *Continued*

7    $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

8    $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-\left(\underset{CH_3}{\underset{|}{CH}}-CH_2-O\right)_{n}\underset{O}{\underset{\|}{C}}-CH=CH_2$

9    $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

10   $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-CH_2 \cdots CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

11
12   $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-\left(CH_2-CH_2-O\right)_{2}-\left[H\right]-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\left[H\right]-O-\left(CH_2-CH_2-O\right)_{2}\underset{O}{\underset{\|}{C}}-CH=CH_2$

13   $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-\left(\underset{CH_3}{\underset{|}{CH}}-CH_2-O\right)_{2}-\left[H\right]-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\left[H\right]-O-\left(CH_2-\underset{CH_3}{\underset{|}{CH}}-O\right)_{2}\underset{O}{\underset{\|}{C}}-CH=CH_2$

$CH_2=CH-\underset{O}{\underset{\|}{C}}-O-\left(CH_2-CH_2-O\right)_{2}-\bigcirc-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\bigcirc-O-\left(CH_2-CH_2-O\right)_{2}\underset{O}{\underset{\|}{C}}-CH=CH_2$

14   $CH_3-CH_2-\underset{\underset{CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2}{|}}{\overset{CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH_2}{\overset{|}{C}}}-CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

15   $CH_3-CH_2-\underset{\underset{CH_2-O-CH_2CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2}{|}}{\overset{CH_2-O-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH_2}{\overset{|}{C}}}-CH_2-O-CH_2CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

16   $CH_3-CH_2-\underset{\underset{CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-\underset{O}{\underset{\|}{C}}-CH=CH_2}{|}}{\overset{CH_2-O-CH_2-\overset{CH_3}{\overset{|}{CH}}-O-\overset{O}{\overset{\|}{C}}-CH=CH_2}{\overset{|}{C}}}-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

17   $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-CH_2-\underset{\underset{CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2}{|}}{\overset{CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH_2}{\overset{|}{C}}}-CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

18   $CH_2=CH-\underset{O}{\underset{\|}{C}}-O-CH_2-\underset{\underset{CH_2}{\underset{|}{\overset{|}{\underset{O-\underset{O}{\underset{\|}{C}}-CH=CH_2}{}}}}}{\overset{HO-CH_2}{\overset{|}{C}}}-CH_2-O-CH_2-\underset{\underset{CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2}{|}}{\overset{CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH_2}{\overset{|}{C}}}-CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH_2$

Table II   PVC Samples Used

Grade	Composition	DP
GEON 25	Homopolymer	850
GEON 135J	Homopolymer	1200
GEON 121	Homopolymer	1650
GEON 43A	Homopolymer	1800
GEON 43H	Homopolymer	3500
GEON 101EP	Vinyl chloride-vinyl acetate copolymer	1450

The samples were supplied by Nippon Geon. DP, degree of polymerization.

Tokyo) or other PVC stabilizers was also added to it. If necessary, inorganic fillers such as calcium carbonate (Shiraishi Calcium Co., Tokyo) were added to the resultant plastisol for the purposes of cost reduction and improvement of the mechanical properties.

Hardening and Curing of Plastisol

The plastisol was placed in a certain mold preheated to the temperature used for molding. The mold was then placed into an oven or a compression molding machine that was preheated to 80–150°C, depending on the reactivity of the peroxide and monomers used. The curing was continued for 5–30 min. Then the mold was taken out and cooled down. The cured resin was finally taken out of the mold.

Molding of SMC

The plastisol was spread over a polypropylene film, and a certain amount of chopped strands of glass fiber (Asahi Glass Co., Tokyo) was placed uniformly on it. It was covered with another polypropylene film and weakly pressed so the glass fiber was wetted with plastisol. It was then heated in an oven at 80°C for 10 min to obtain an SMC sheet in the so-called B stage.

Then the SMC sheet obtained was put on a hot mold and compressed with a compression molding machine at 150°C by applying a pressure of 100–150 kg/cm^2 for 3–5 min. The molded product was then taken out.

Measurements

The viscosity of the plastisol was measured with the Brookfield LVF viscometer equipped with a #4 spindle at 23°C according to ASTM D1824.[6] The stability of the plastisol was estimated by the viscosity change. When the viscosity of the plastisol was kept at less than 3 times the initial viscosity even after passing 10 h after preparation at 23°C, the stability was judged to be good. The hardness of the cured resin was measured with a shore D hardness tester according to ASTM D2240[7] by utilizing a 30-mm diameter and 5-mm thickness disk sample. The specific gravity was measured according to ASTM D792.[8] The flexural strength and modulus were measured on a Shimadzu Auto Graph AG-10TC according to ASTM D790.[8] The heat distortion temperature (HDT) was measured according to ASTM D648[8] with a strip sample of 12.7 × 140 × 3 mm (width × length × thickness).

RESULTS AND DISCUSSION

Screening of Acrylates as Plasticizer

The common plastisols consisting of PVC and plasticizer change their form from liquid to solid (B stage) on heating. During this phase change, plasticizer (liquid) is allowed to penetrate into PVC particles (solid) and induce solidification of the plastisol without an accompanying chemical

Table III   Peroxides Used

Peroxide	Abbreviation	Half-Life Time	
		at 80°C (h)	at 150°C (s)
t-Butyl peroxyoctanoate	TBO	10	50
t-Butyl peroxybenzoate	TBB	20	120
Dicumylperoxide	DCP	80	180
Di-*t*-butylperoxide	DBP	100	7200

The peroxides were supplied by Nippon Yushi Co. Ltd.

Table IV   Results of Screening Test of Acrylates

	Acrylate		SP (cal/ cm^3)$^{1/2}$	Viscosity (mPas)		B-Stage Formation
Run	Type	Name (MW)		As Mixed	After 5 h	
1	Monoacrylate	HEMA (130)	12.9	Gel	—	—
2		GMA (142)	9.8	Gel	—	—
3		EHA (184)	8.6	250	250	No
4		NVP (111)	11.4	Gel	—	—
5		THFA (156)	9.5	Gel	—	—
6		DCPDA (204)	9.7	1,200	1,300	No
7	Diacrylate	NPDA (212)	9.4	450	500	No
8		PPA (358)	8.9	700	700	No
9		NPPA (328)	9.2	650	700	Yes
10		TCDA (304)	9.9	650	700	Yes
11		HBEA (524)	9.3	1,100	1,200	Yes
12		HBPA (552)	9.1	2,900	3,300	Yes
13		BPEA (512)	10.2	4,800	5,200	Yes
14	Triacrylate	TMPA (296)	9.9	750	800	Yes
15		TMPEA (428)	9.8	950	1,100	Yes
16		TMPPA (456)	9.5	1,100	1,200	Yes
17	Tetraacrylate	PETA (352)	9.8	1,200	1,250	Yes
18	Pentaacrylate	DPHA (578)	10.4	14,000	15,000	Yes

SP, solubility parameter.

reaction. The reactive plastisol incorporated into the acrylate monomers as a plasticizer should not only keep this hardening nature but also allow curing by vinyl polymerization of the plasticizer after the solidification. Figure 1 shows the outline of the processing of the reactive plastisol compared with that of the ordinary plastisol. In the former the B-stage product, which was hardened

Figure 1   A comparison of plastisol and reactive plastisol.

at a relatively lower temperature, is subjected to postcuring in which product shaping is also conducted. Because most plasticizers consist of esters of multifunctional acids and alcohols of medium carbon chain length, the acrylates of the mono- and polyhydroxy compounds having an appropriate carbon number should be structurally similar to them and show a good plasticizing effect on PVC. Furthermore, the acrylates can incur radical polymerization in the postcuring stage. Therefore, the formulation of reactive plastisol should largely depend on what acrylate is used as the polymerizable plasticizer.

Table IV shows the results of the screening test of the acrylates used as the polymerizable plasticizers. The test was done at a PVC/acrylate composition of 50/50 (w/w) with various acrylate monomers (mono-, di-, and polyfunctional) whose solubility parameters vary from 8.6 to 12.9.[8] The criteria of evaluation were on the following points: whether the resulting plastisol was kept stable or fluid at room temperature for at least several hours after preparation as measured by viscosity change, whether the sol turns to the B stage in a short time (10 min) at around 80°C, and whether the B-stage product can be stored long term. On mixing with HEMA (run 1), GMA (run 2), NVP (run 4), and THFA (run 5), the PVC
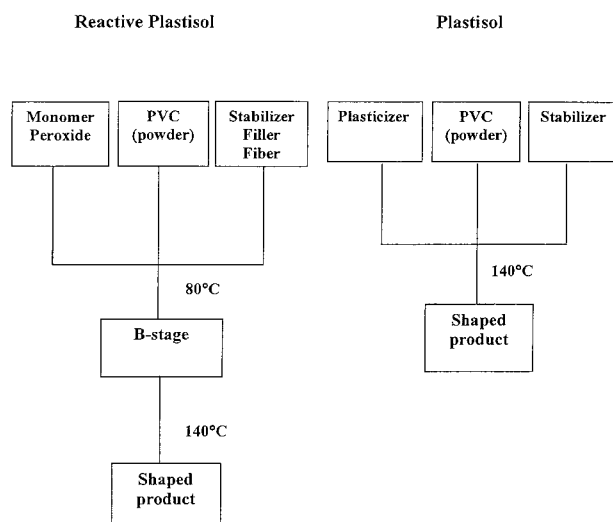
Table V   Effect of PVC Grade on Properties of Reactive Plastisols and Their Cured Sheets

	Run					
	10-1	10-2	10-3	10-4	10-5	10-6
GEON 25 (wt %)	50	—	—	—	—	—
GEON 135J (wt %)	—	50	—	—	—	—
GEON 121 (wt %)	—	—	50	—	—	—
GEON 43A (wt %)	—	—	—	50	—	—
GEON 43H (wt %)	—	—	—	—	50	—
GEON 101EP (wt %)	—	—	—	—	—	50
TCDA (wt %)	50	50	50	50	50	50
TBB (wt %)	0.5	0.5	0.5	0.5	0.5	0.5
Zinc stearate (wt %)	0.5	0.5	0.5	0.5	0.5	0.5
Viscosity of plastisol (mPas)	600	700	650	340	260	—
Stability of plastisol[a]	G	G	G	G	G	N
B-stage formation[b]	G	G	G	G	N	—
Specific gravity	1.225	1.226	1.226	1.227	1.226	—
Flexural modulus (MPa)	340	350	380	400	410	—
Flexural strength (MPa)	10.4	10.8	11.5	13.3	14.8	—
HDT (°C)	97	98	98	98	98	—
Shore D hardness	86	86	88	89	88	—

[a] G, the plastisol maintained liquid form longer than 10 h; it turned to solid within 10 h after the preparation.
[b] G and N, the plastisol did and did not solidify, respectively, by heating at 80°C for 10 min.

particles were conglomerated because of their fast solvation. (Refer to Tables I and III for names of compounds abbreviated in the text). For the PVC mixtures with the other acrylates (runs 9–18), little viscosity change was observed 5 h after the mixing. On the other hand, EHA (run 3), DCPDA (run 6), NPDA (run 7), and PPA (run 8) did not form a stable B-stage because of their poor compatibility with PVC. The poor compatibility of PPA may probably be attributed to poly(oxypropylene) chain. With other diacrylates such as HBEA (run 11) a similar result was obtained, while the plastisols containing HBPA (run 12) and BPEA (run 13) were too viscous to carry out their processing. The plastisols consisting of tri-(TMPA) (run 14), tetra- (PETA) (run 17), and pentaacrylates (DPHA) (run 18) as plasticizers likely formed cracks when curing because of the excessive crosslinking and the concomitantly induced large shrinkage. On the other hand, such triacrylates as TMPEA (run 15) and TMPPA (run 16) gave cured sheets with good quality. This is because of the plasticizing effect of the oxyethylene (EO) or oxypropylene (PO) unit in the molecule.

These results suggest that the acrylates of diols and polyols with medium chain length can form stable plastisols that can form the stable B stage by

heating. The chemical structure of the original diols and polyols of the effective acrylates seems to be less important if they are nonvolatile and have high molecular weight. Neither the solubility parameter of the acrylates [9.1–10.4 $(cal/cm^3)^{1/2}$ for the effective acrylates] nor the presence of EO and PO units in the original diols and polyols show a close relationship with the performance of the resultant plastisols. The molecular weight or viscosity of the acrylates may become more important factors for selecting the plasticizer.

Screening of PVC

Table V shows the typical properties of the reactive plastisols comprising PVC with different degrees of polymerization (DP) and copolymer composition. TCDA was used as one of the most effective plasticizers. The viscosity of the plastisols decreased with an increasing DP of PVC because of the decreasing affinity of the plasticizer with the increasing DP (runs 10-1–10-4). However, the plastisol comprising PVC with the highest DP (3500) did not turn into the B stage at 80°C, although it hardened at the curing temperature (run 10-5). The copolymer (GEON 101EP) of vinyl chloride and vinyl acetate gave an unstable plastisol because it had a good affinity with TCDA

Table VI   Effect of Peroxide on Properties of Plastisols

	Run			
	10-7	10-8	10-9	10-10
TBO (wt %)	0.5	—	—	—
TBB (wt %)	—	0.5	—	—
DCP (wt %)	—	—	0.5	—
DBP (wt %)	—	—	—	0.5
B-stage formation (80°C, 10 min)	Reaction started	Good	Good	Good
Curing (150°C, 10 min)	Good	Good	Not enough	Not enough

For this plastisol the GEON 43A was mixed with 50 wt % TCDA and 0.5 wt % zinc stearate.

(run 10-6). The flexural modulus and strength of the finally hardened sheet increased with the increasing DP of PVC. These data suggest that PVC with a DP of 1800 should be the best in the formulation of the plastisol (run 10-4).

Screening of Peroxide

Peroxide was incorporated into the plastisol for the initiation of radical polymerization of the acrylates in the curing stage. The effects of the representative peroxides on the formulation of the plastisol are compared in Table VI. For the sheet molding compounds the peroxide should not decompose during the formation of the B stage but it should decompose immediately on reaching 140–180°C, which

initiates the radical polymerization of the acrylates. Because the half-life of TBO at 80°C was too short, the plastisol containing TBO was allowed to harden during the formation of the B stage by concominant polymerization of the acrylate (run 10-7). On the other hand, DCP (run 10-9) and DBP (run 10-10) whose half-life at 150°C was too long did not induce the hardening in the curing stage. Only TBB was found to have adequate half-lives at 80 and 150°C, which gave good results in forming the B stage and in curing (run 10-8).

Evaluation of Plastisols with Different Formulations

PVC with a DP of 1800 was used to formulate various plastisols with a mixture of TCDA and

Table VII   Effect of Formulation on Properties of Reactive Plastisols and Their Cured Sheets

	Run			
	10-11	10-12	10-13	10-14
GEON 43A (wt %)	50	50	50	50
TCDA (wt %)	50	40	30	20
NPDA (wt %)	0	10	20	30
TBB (wt %)	0.5	0.5	0.5	0.5
Zinc stearate (wt %)	0.5	0.5	0.5	0.5
Viscosity of plastisol (mPas)	340	230	200	180
Stability of plastisol[a]	G	G	G	G
B-stage formation[b]	G	G	G	G
Specific gravity	1.227	1.225	1.222	1.221
Flexural modulus (MPa)	400	390	400	410
Flexural strength (MPa)	13.3	14.0	14.2	13.8
HDT (°C)	98	115	120	125
Shore D hardness	89	90	90	91

[a,b]Refer to the footnotes of Table V.

Table VIII   Physical Properties of SMC and Cured FRP

	Run				
	10-5	10-5G	11-1G	10-12G	10-12H
GEON 43A (wt %)	50	50	50	50	50
TCDA (wt %)	50	50	—	30	30
HBEA (wt %)	—	—	50	—	—
NPDA (wt %)	—	—	—	20	20
TBB (wt %)	0.5	0.5	0.5	0.5	0.5
Glass fiber (wt %)	—	60	60	60	100
Zinc stearate (wt %)	0.5	0.5	0.5	0.5	0.5
Specific gravity	1.227	1.332	1.350	1.348	1.482
Flexural modulus (MPa)	400	1340	1380	1400	1620
Flexural strength (MPa)	13.3	37	39	34	45
HDT (°C)	98	>200	>200	>200	>200

NPDA as the plasticizer. The results are summarized in Table VII. Although the plastisol containing only NPDA did not form a stable B stage (run 7), those containing the mixture could form a stable B stage and give a good quality cured sheet. The viscosity of the latter plastisols became lower with the increase in composition of NPDA, while the flexural modulus and strength of the cured sheet were maintained constant irrespective of the composition. Another merit of mixing TCDA and NPDA is that the HDT of the cured sheet increased with the increasing composition of NPDA.

Properties of FRP Prepared Via SMC

The potentially good plastisols selected in the above screening tests were subjected to processing FRP via the SMC molding. The typical results are shown in Table VIII. The plastisols comprising TCDA (run 10-5G) and HBEA (run 11-1G), as well as a mixture of TCDA and NPDA [30/20 (w/wt), run 10-12G60], were impregnated into 60 w% of chopped glass fiber to give processable SMC sheets. The flexural modulus and strength of the finally obtained FRP were about 3 times those of the cured sheets of the original plastisols without mixed glass fiber. Because the viscosity of the plastisol comprising the TCDA/NPDA mixture was low, 100 wt % glass fiber could be impregnated with it to give a much harder and tougher sheet (run 10-12G100). These data supported the idea that FRP can be made by a combination of the plastisol with glass fiber and by the application of the conventional SMC procedure.

CONCLUSION

A new type of plastisol, reactive plastisol, was developed by incorporating polyfunctional acryl mono-

mers into PVC powder as plasticizers. This class of acrylate-modified plastisols can be hardened into the B stage and then cured into a harder material through crosslinking of the acrylate. The evaluation of various acrylates revealed that difunctional acrylates such as TCDA and HBEA can be the most conveniently used plasticizers. A mixture of TCDA and NPDA yields a less viscous plastisol that can be readily impregnated into a glass fiber. An SMC was obtained by the combination of the plastisol with glass fiber by compression molding using conventional machines. It was cured into a PVC-based FRP with higher performance compared to the conventional unsaturated polyester-based FRP.

REFERENCES

1. Plastisols, Encyclopedia of Chemical Technology, 3rd ed.; Wiley: New York, 1983; Vol. 23, p 922.
2. Plastisols, Encyclopedia of Polymer Science and Technology; Wiley: New York, 1971; Vol. 14, p 370.
3. Nakajima, N.; Sadeghi, M. R.; Kyu, T. J Appl Polym Sci 1990, 41, 889.
4. Nakajima, N.; Daniels, C. A. J Appl Polym Sci 1980, 25, 2019.
5. (a) Fedors, R. F. Polym Eng Sci 1974, 14, 147; (b) Fedors, R.F. Polym Eng Sci 1974, 14, 472.
6. Annual Book of ASTM Standards; American Society for Testing and Materials: Philadelphia, PA, 1992; Vol. 08.02.
7. Annual Book of ASTM Standards; American Society for Testing and Materials: Philadelphia, PA, 1992; Vol. 08.03.
8. Annual Book of ASTM Standards; American Society for Testing and Materials: Philadelphia, PA, 1992; Vol. 08.01.