

Recycling of Sheet-Molding Compounds by Chemical Routes

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SYNOPSIS

This article describes a number of chemical routes for the recycling of sheet-molding compounds (SMC) consisting of glass fibers, filler (calcium carbonate), and an unsaturated polyester-styrene thermoset resin. Treatment of milled SMC with ethanol/potassium hydroxide at 85°C for 48 h ultimately affords a soluble polymeric fraction, consisting of styrene-fumaric acid copolymers. The excess of potassium hydroxide as well as the filler are removed via a neutralization step, which results in a large stream of waste chemicals. Treatment of SMC chips with ethanolamine at 180°C for 48 h gives a reaction mass that can be split into three fractions, viz., the glass fibers, the filler, and a methanol-soluble polymeric residue. The excess of ethanolamine is recovered by distillation at 220°C and reduced pressure. The polymeric fraction consists of terpolymers of styrene, *N,N'*-di(2-hydroxyethyl)fumaramide and *N*-2-hydroxyethylmaleimide monomer units, the latter two bearing two and one hydroxyl groups, respectively. The terpolymer shows little solubility in unsaturated polyester, epoxy, or isocyanate resins. The glass fibers and the filler coated with the polymeric fraction can be used as constituents of bulk-molding compounds (BMC). Replacing half of the original amount of glass fibers or filler of a standard BMC formulation by recycled materials does not significantly alter the mechanical properties. Increasing the amount of recycle results in processing difficulties in the case of the glass fibers or a serious decline of the mechanical properties in the case of the filler/polymer. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Recycling of car components becomes increasingly important. Whether metals or polymers should be used to construct a car depends, among others, on the possibility to reuse the material of choice. Both thermoplastic and thermosetting polymers are being applied, e.g., polypropylene (PP) compounds in car bumpers and sheet-molding compounds (SMC) in motorhoods.

In the case of PP bumpers, recycling seems to be straight-forward as regrain can be extruded to make compounds again. However, degradation during processing and the presence of paint particles affect the properties of the recycle. Such problems should be dealt with in order to prove that recycling is feasible.

Thermosets cannot be melt-processed after being cured. SMC consists of roughly 70 wt % of inorgan-

ics, viz., calcium carbonate (filler) and glass fibers, and 20–25 wt % of an unsaturated polyester/styrene (UP) thermoset resin. Important additives are thickeners, usually magnesium oxide, 5–10 wt % of a thermoplastic to provide a smooth surface (low-profile additive), and an initiating system. Copolymerization of the unsaturated polyester and styrene by a radical mechanism generates a C—C polymer backbone connected by the polyester chains (Fig. 1).

There are at least two routes for the recycling of SMC-based car components. One option is to apply ground material as a partial replacement for filler and glass fibers. Another possibility involves the selective degradation of the polyester-styrene polymer network by reaction of the ester linkages with an appropriate nucleophile. In fact, Funke et al. showed that reactions of well-ground, unfilled UP resin with potassium hydroxide/benzyl alcohol, hydrazine, or benzylamine afford soluble copolymers of styrene and fumaric acid derivatives.¹ Neutral hydrolysis of the ester linkages, as proposed by Tesoro et al., appeared to be even more promising.² Reaction of well-

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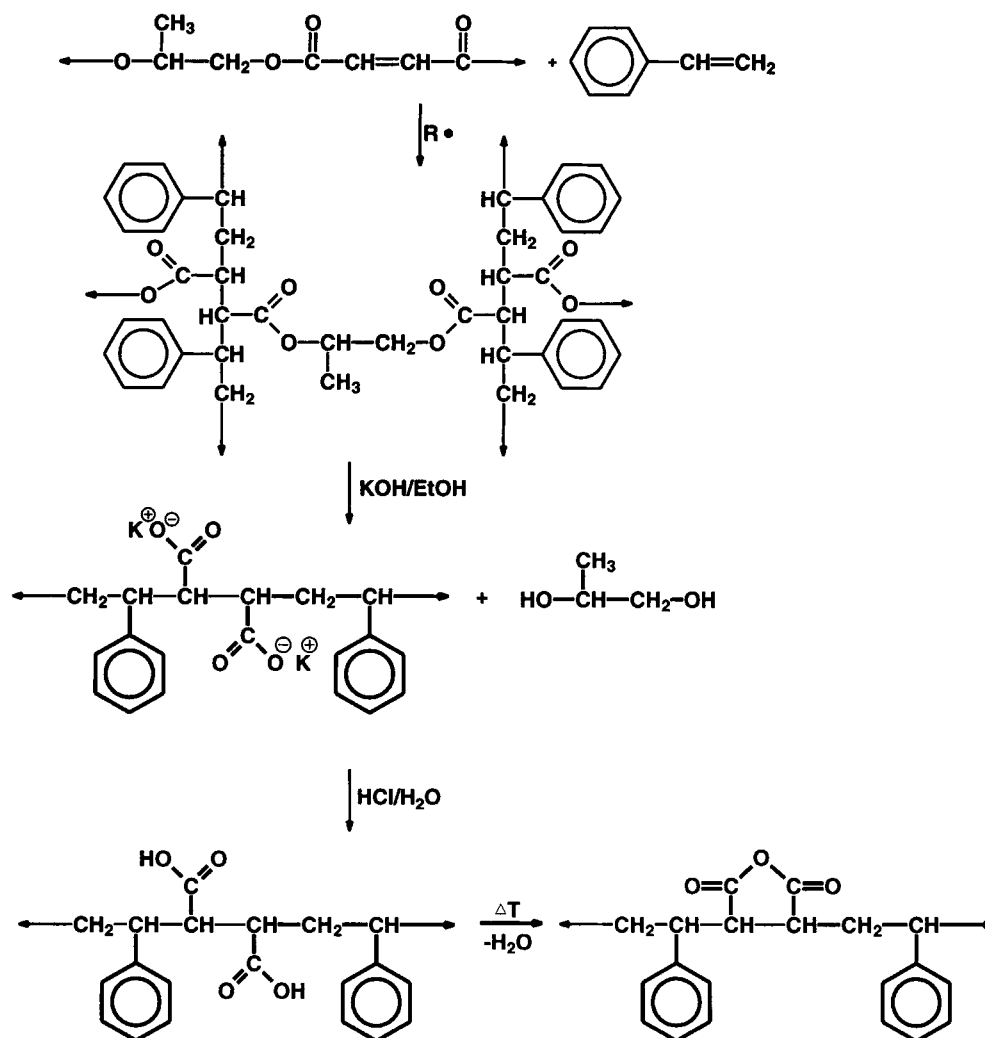


Figure 1 Selective degradation of the polyester-styrene network using potassium hydroxide and ethanol at 85°C.

ground, unfilled UP resin with water at 240–275°C and 40–65 bar for 2–6 h resulted in carboxylic acid containing oligomers and additional monomers.

However, little is known about the chemical recycling of SMC. In this respect, a major problem is to recover not only the organic part of SMC, but also the glass fibers and filler in such a way that they can be reused. This report describes the selective degradation of SMC in the presence of water, ethanol, potassium hydroxide, and various amines.

EXPERIMENTAL

Materials

SMA-3000 (Atochem), UP-S-423 (DSM Resins), SMC-A (ERCOM), ethanol (Riedel-de Haen), potassium hydroxide (Merck), hydrochloric acid

(Merck), methyl ethyl ketone (Riedel-de Haen), tetrahydrofuran (Baker), $DMSO-d_6$ (Aldrich), sodium hydroxide (Merck), diethyl succinate (DES, Janssen), ethanolamine (EA, Baker), diethanolamine (DEA, Janssen), benzylamine (BA, Janssen), benzylamine hydrochloride (Janssen), 2-methoxy-ethylamine (Janssen), bis(methoxyethyl)amine (Aldrich), 1-amino-2-propanol (AP, Janssen), 1-amino-2-methyl-2-propanol (AMP, Janssen), 2-(methylamino)ethanol (MAE, Janssen), chloroform (Baker), and methanol (Riedel-de Haen) were used as received. Also, see Table I.

Methods

The 1H - and ^{13}C -NMR spectra were recorded with a Bruker ACF200 and a Varian Unity 300 spectrometer, respectively, under standard conditions. IR

Table I Composition of SMC-A and SMC-B

	SMC-A (Wt %)	SMC-B (Wt %)
Unsaturated polyester ^a	10	10
Low-profile additive ^b	5	6
Styrene	12	7
Calcium carbonate	45	43
Glass fibers	25	27
Additives ^c	3	7

^a Propylene glycol/maleic anhydride polyester.

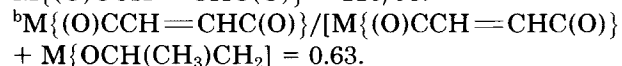
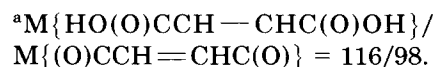
^b Polyester (SMC-A) or polystyrene (SMC-B).

^c Initiator/accelerator, thickener (MgO), pigment.

spectra were recorded on Perkin-Elmer equipment using KBr pills. The gel-permeation chromatography (GPC) equipment consisted of a Rheodyne injector, a Gilson 302 pump, a Gilson Holochrome UV detector (wavelength 254 nm), and 100, 500, 1000 and 10,000 Å Styragel columns. Calibration was carried out with polystyrene samples. Cured UP

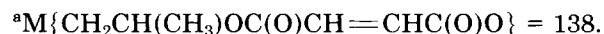
Wt % extractable polymer after working-up procedure

$$\begin{aligned}
 &= \frac{116/98^a \times 0.63^b \times \text{wt \% UP (SMC-A)} + \text{Wt \% ST (SMC-A)}}{116/98 \times 0.63 \times \text{wt \% UP (SMC-A)} + \text{wt \% ST (SMC-A)} + \text{wt \% glass (SMC-A)}} \times 100\% \\
 &= \frac{116/98 \times 0.63 \times 10 + 12}{116/98 \times 0.63 \times 10 + 12 + 25} \times 100\% = 45 \text{ wt \%}
 \end{aligned}$$



Mol % succinic acid units

$$\begin{aligned}
 &= \frac{\text{wt \% UP (SMC-A)} / 138^a}{\text{wt \% UP (SMC-A)} / 138 \\
 &+ \text{wt \% ST (SMC-A)} / 104} \\
 &\times 100\% = \frac{10/138}{10/138 + 12/104} \times 100\% = 38 \text{ mol \%}
 \end{aligned}$$



Reactions of DES with EA, DEA, and BA

All reactions were carried out in the same way. The following procedure serves as an example: Ten grams (0.057 mol) of DES and 14.0 g (0.230 mol) of EA were stirred at 100°C. After a specified period of

(UP-S-423), SMC-B, and BMC samples were prepared and subsequently processed according to standard techniques.

Solvolysis of SMC-A in the Presence of Ethanol/Potassium Hydroxide

All experiments were performed in the same way. The following procedure serves as an example: Six hundred grams of SMC-A powder was stirred in a solution of 250 g of potassium hydroxide in 1250 g of ethanol for 48 h at 85°C. The resulting solid mass was filtered, subsequently washed with ethanol, and dried at 80°C *in vacuo*. Neutralization by boiling with 600 mL of 37% hydrochloric acid during 3 h, subsequent washing with water, and drying at 80°C gave 256 g of a gray solid material. Extraction of a sample of this material with methyl ethyl ketone using a Soxhlet equipment showed that 38 wt % could be dissolved (ST = styrene):

time, a sample was withdrawn from the reaction mixture, dissolved in DMSO-*d*₆, and subsequently analyzed using ¹H-NMR.

Reactions of UP Resin Granulate with Various Ethanolamines

All reactions were carried out in the same way. The following procedure serves as an example: UP-S-423 granulate, 20.6 g (< 5 mm), and 40.7 g of EA were heated at 180°C. After a specified period of time, the reaction mixture was diluted with 500 mL of methanol and subsequently filtered to determine the amount of insoluble material.

Reaction of DES with EA at 180 and 220°C

A mixture of 30 g (0.17 mol) of DES and 42.1 g (0.68 mol) of EA was stirred at 180°C for 30 min, during which 13.5 g (0.29 mol) of ethanol was distilled (theoretical amount 15.9 g). Thereafter, the mixture was heated at 220°C and 60 mmHg. After 6 h, the

brown oil was cooled to room temperature, dissolved in water, and subsequently extracted with chloroform. Evaporation of the solvent gave a small amount of a gray solid, *N*-(2-hydroxyethyl) succinimide, according to the ¹H-NMR spectrum (Fig. 4).

Solvolysis of SMC-B in the Presence of EA

In a 2 L polymerization vessel, 1000 g of SMC-B pieces (1 × 3 × 0.4 cm³) and 570 g of EA were heated under reflux conditions for 48 h. The reaction mass was poured onto a wide-pore filter (1 mm² pore size) to separate the glass fibers. Several washings with methanol and drying *in vacuo* at 60°C gave 266 g of visually clean fibers. Filtration of the heterogeneous remainder gave a gray solid (filler) that was dried *in vacuo* at 60°C and subsequently powdered to 441 g. Distillation of the filtrate at 120°C (3 h) and 220°C (3 h) (60 mmHg) resulted in 290 g of a red-brown solid.

RESULTS AND DISCUSSION

Solvolysis of SMC in the Presence of Water or Ethanol

As the first step, we investigated a commercial-grade SMC analogous to the work of Funke et al. on unfilled UPs.¹ The SMC-A (see Experimental) used in our study contains a rather simple unsaturated polyester prepared from maleic anhydride and propylene glycol, while the low-profile additive is composed of propylene glycol, ethylene glycol, and adipic acid.

Finely ground SMC-A was heated in potassium hydroxide/ethanol at 85°C for a specified period of time. The solid mass was separated by filtration and subsequently washed with ethanol to remove low molecular weight compounds. Treatment of the reaction product with hydrochloric acid resulted in the removal of calcium carbonate (filler) and the transformation of the potassium carboxylate groups into carboxylic acid groups (Fig. 1). Extraction of the remainder with methyl ethyl ketone gave a soluble polymer fraction, the number-average molecular weight M_n , the weight-average molecular weight M_w , and the dispersion D ($D = M_w/M_n$), which were determined using GPC. All results are compiled in Table II.

Assuming complete conversion, one can calculate the theoretical amount of extractable polymer (see Experimental part). After the working-up procedure,

Table II Selective Degradation of SMC-A with Potassium Hydroxide and Ethanol at 85°C

<i>T</i> (h)	Extracted Polymer (Wt %)	Conversion (%)	M_w	M_n	<i>D</i>
7	11	25	14,000	1200	11.7
35	31	70	6,100	600	10.2
48	38	86	6,700	650	10.3

the SMC remainder should contain 56 wt % of glass and 44 wt % of soluble polymer. Table II indicates that under these conditions complete conversion takes more than 48 h. Initially, the soluble polymer fraction most probably consists of branched chains. In the course of the reaction, the C—C backbone and the polyester branches are disconnected, resulting in a decrease of M_n to a constant level of about $M_n = 600$.

These values of M_n suggest that during the peroxide cure of the SMC at temperatures above 150°C relatively short polymer chains are formed. This might be due to an increased concentration of initiator radicals, the occurrence of chain-transfer reactions, or to the dilution of the system by the glass fibers and the filler. The data obtained so far do not allow a firm conclusion to be drawn.

Styrene-maleic anhydride (SMA) copolymers have been the subject of extensive analytical research, which prompted us to characterize our reaction products in more detail.^{3,4} The soluble polymer fraction obtained after 48 h was heated at 180°C for 4 h. The IR spectrum of this material [Fig. 2(C)] appeared to be identical to the one of a commercially available low molecular weight SMA copolymer [SMA-3000, Fig. 2(A)].

A quantitative IR measurement revealed that the copolymer consists of 20 mol % of maleic anhydride and 80 mol % of styrene monomer units. The composition of the untreated copolymer was analyzed using ¹³C-NMR [Fig. 2(D)]. The low-field side of the spectrum shows three broad patterns belonging to the carboxylic acid groups (170–175 ppm), to the C1 of the styrene monomer unit (139–146 ppm), and to the remaining aromatic carbon atoms of the styrene monomer unit (124–130 ppm). From the integration of the quaternary COOH and C1 peaks, one can calculate the composition of the copolymer: 25 mol % of fumaric acid monomer units and 75 mol % of styrene monomer units. The IR and NMR results seem to be in agreement given the difficulties of a quantitative ¹³C-NMR measurement.

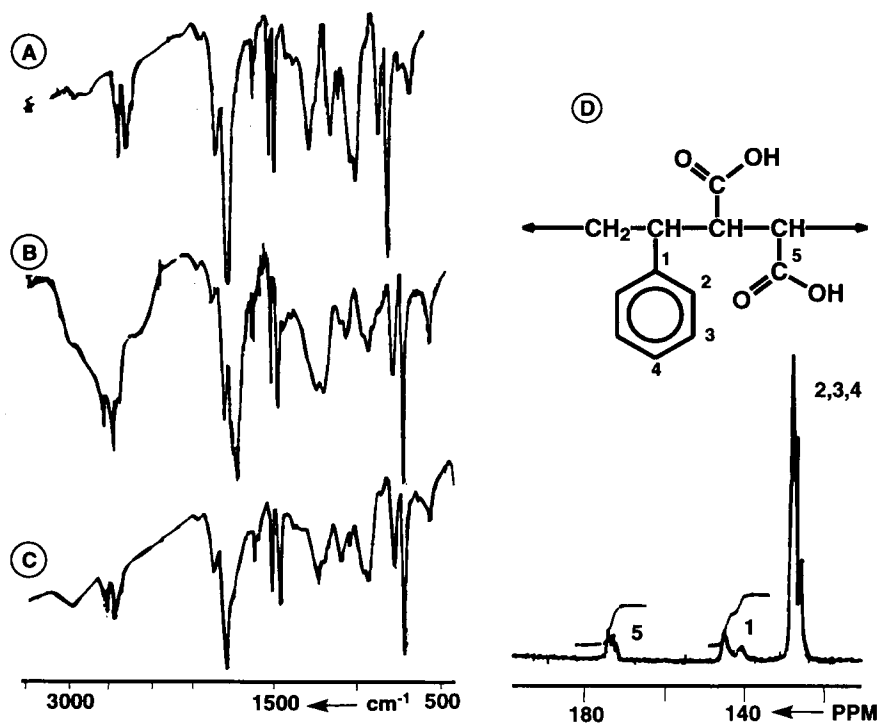


Figure 2 (A) IR spectra of SMA-3000, (B) the solvolysis product, and the solvolysis product after heat treatment at 180°C (C). (D) ^{13}C -NMR spectrum (low-field region) of the solvolysis product in $\text{DMSO}-d_6$.

Calculation of the theoretical composition of the copolymer from the SMC formulation (see Experimental part), assuming that all ester linkages have been converted, gives 38 mol % of fumaric acid monomer units and 62 mol % of styrene monomer units. Hence, the cured SMC still contains unreacted fumaric acid esters. During solvolysis, fumaric acid will be split off and subsequently removed from the reaction product by washing with methanol.

From the results obtained so far, it appears that powdered SMC can be degraded in the presence of potassium hydroxide/ethanol at 85°C. However, from an economical point of view, this method has several disadvantages. In practice, one would choose to treat relatively large pieces of SMC in order to save the glass fibers. Furthermore, potassium hydroxide has a detrimental effect on the glass fibers. In addition, the use of large amounts of potassium hydroxide asks for a neutralization step, which results in a large stream of waste chemicals. Moreover, this procedure also induces the removal of the filler calcium carbonate.

These considerations prompted us to carry out reactions of SMC samples of about $1 \times 1 \times 0.4 \text{ cm}^3$ with water or ethanol and catalytic amounts of sodium hydroxide at high temperatures and high pres-

ures.⁵ The experimental results fall into two categories: Treatment of SMC-A with water under near-supercritical conditions (300–375°C, 80–240 bar) during 10–240 min afforded low molecular weight products from pyrolytic reactions. Reactions with water or ethanol and sodium hydroxide at 150–250°C and 10–100 bar for 60–720 min gave small amounts of extractable material, generally less than 8 wt %.

These results suggest one to look for another, more reactive chemical that can be easily removed afterward when more than equivalent amounts are used. This chemical should also be less aggressive toward glass fibers. We decided to evaluate amines, in particular ethanolamines, as potential reagents for the selective degradation of SMC.

Solvolysis of SMC in the Presence of Ethanolamines

The potential of amines to solvolyse SMC was investigated via reactions of a model compound, viz., diethyl succinate (DES) with ethanolamine (EA), diethanolamine (DEA), and benzylamine (BA). The latter reagent was also used by Funke et al. for the analysis of unfilled UPs.¹

Reaction mixtures of DES and the amine, molar ratio 1 : 4, were stirred at 100°C for a specified period of time. The conversion of ester groups was followed by ¹H-NMR. The experimental results are visualized in Figure 3.

In the case of BA, 5 mol % of the hydrochloric acid derivative of BA was used as a catalyst, because BA itself did not react. Figure 3 shows that there is a considerable gap between BA and the ethanolamines EA and DEA, of which EA is the most reactive one. It is known that protic solvents impart an accelerating effect on amidation reactions.⁶ The hydroxyl group of EA probably acts in the same way. Experimental evidence was obtained by reacting DES with the methoxylated derivatives of EA and DEA, viz., 2-methoxyethylamine and bis(methoxyethyl)amine. Both amines showed no reactivity toward DES under the circumstances used for EA and DEA.

Besides DEA and EA, various other ethanolamines exist that are commercially available, viz., 1-amino-2-propanol (AP), 1-amino-2-methyl-2-propanol (AMP), and 2-(methylamino)ethanol (MAE). In contradistinction to MAE and AP, AMP did not react with DES at 100°C, probably due to steric hindrance.

In the next step, cured UP resin (granulate < 5 mm) was dissolved at 180°C in the presence of two equivalents of EA, DEA, AP, or MAE per ester linkage for 4, 8, and 24 h.

The effectiveness of a particular amine was determined as the amount of methanol-insoluble material. The experimental results (Table III) indicate that the primary amines EA and AP are more reactive than are the secondary ones: MAE and DEA. EA is slightly more reactive than is AP, particularly in the beginning of the reaction. On the basis of these results, we took EA as the reagent of choice for further experiments.

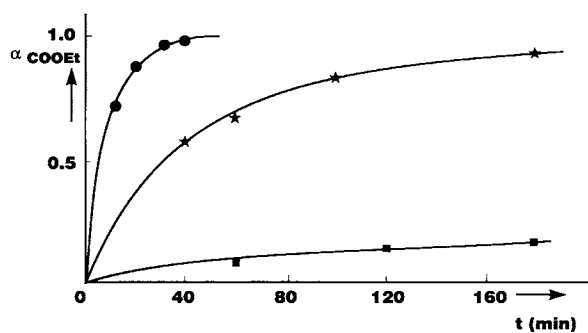


Figure 3 Reactions of DES with four equivalents of (○) EA, (*) DEA, or (□) BA/BA·HCl (0.05) at 100°C.

Table III Reactions of Cured UP Resin (Granulate < 5 mm) with MAE, DEA, AP, or EA, 2 Equivalents per Ester Linkage, at 180°C

	t (h)	Wt % Insoluble (Methanol)
MAE	4	64
	8	67
	24	56
AP	4	33
	8	28
	24	7
DEA	4	86
	8	37
	24	31
EA	4	9
	8	12
	24	12

Beforehand, it was expected that solvolysis of SMC chips requires an excess of EA in order to induce proper wetting of the material. As a consequence, the excess of EA needs to be removed by distillation together with the reaction product propylene glycol. After dissolving the granulated UP, the distillation temperature at 60 mmHg was raised to 220°C to obtain EA-free material. Possible side reactions at this temperature were investigated by using DES.

Reaction of DES with four equivalents of EA at 180°C gave *N,N'*-di(2-hydroxyethyl)succinamide in quantitative yield under distillation of ethanol. During heating at 220°C and 60 mmHg, under distillation of EA, samples were taken from the reaction mixture and subsequently analyzed using ¹H-NMR. Initially, the reaction mixture contained the diamide and EA [Fig. 4(A)]. After 30 min, a symmetrical derivative of the diamide was formed as indicated by the singlet at 2.6 ppm [Fig. 4(B) and (C)]. The fact that EA was still being distilled suggests that *N*-(2-hydroxyethyl succinimide) is formed by splitting off EA. The kinetic results are shown in Figure 5. After 6 h at 220°C, the reaction mixture was cooled to room temperature and dissolved in water. Extraction with chloroform resulted in the isolation of a small amount of a gray solid, the ¹H-NMR spectrum of which is displayed in Figure 6. The spectrum shows three sets of signals at 4.7, 3.4, and 2.6 ppm, respectively, with an integration ratio of 1.0 : 4.0 : 4.0. The singlet at 2.6 ppm indicates that a symmetrical derivative of the diamide is formed. The distorted triplet at 4.7 ppm points to the pres-

Table IV Mechanical Properties of BMC (Three-point Bending ASTM-D-790M, Charpy ISO-179) upon Replacing Part of the Constituents by Recycled Material (A = Standard Formulation)

Composition	A (Parts)	B (Parts)	C (Parts)	D (Parts)
Synolite 401-A-1	50	50	50	50
Synolite 1080-40	10	10	10	10
Millicarb	55	55	27.5	—
Recycled filler/polymer	—	—	27.5	55
Glass R 63 DX3 (13 mm)	28	14	28	28
Recycled glass	—	14	—	—
Additives	5	5	5	5
Mechanical properties				
E-mod (GPa)	14 (1)	13 (1)	10 (1)	6 (1)
Flexural strength (MPa)	80 (30)	86 (10)	65 (20)	40 (10)
ϵ (flex) (%)	1 (0.3)	1 (0.2)	1 (0.2)	1 (0.2)
Charpy (kJ/m ²)	21 (9)	13 (5)	14 (7)	10 (4)

ence of an OH group: one OH group per C(O)CH₂CH₂C(O) moiety according to peak integration. The multiplet at 3.4 ppm represents four protons. On the basis of these considerations, we

concluded that the reaction product consists of *N*-(2-hydroxyethyl)succinimide.

Solvolysis of cured UP resin at 180°C for 24 h followed by distillation of the excess of EA for 3 h

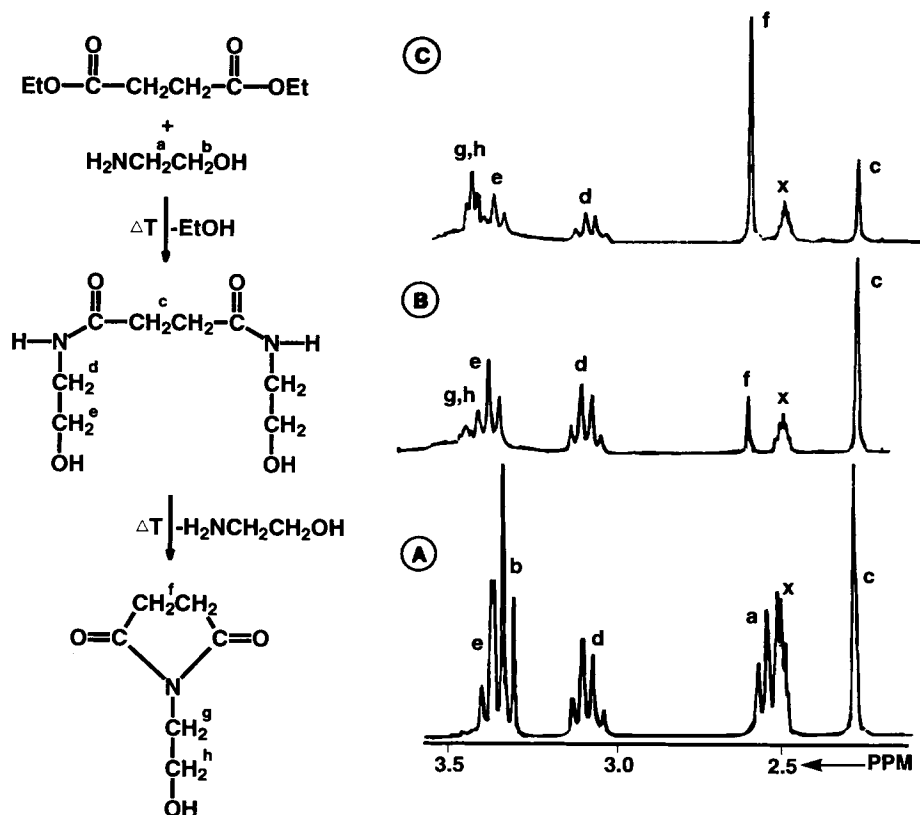


Figure 4 Reaction of DES with four equivalents of EA at 180 and 220°C. ¹H-NMR spectra (DMSO-*d*₆) of the reaction mixture after (A) 0, (B) 30, and (C) 90 min at 220°C.

at 120°C (60 mmHg) and, finally, 3 h at 220°C (60 mmHg) gave a red-brown syrup that solidified at room temperature. Nitrogen elemental analysis gave a value of 7.7 wt % N, while the OH number amounted to 327 mg KOH per g. The original UP resin contains 65 wt % of a propylene glycol-maleic anhydride polyester and 35 wt % of styrene. Assuming that all styrene has reacted, one can calculate the nitrogen content and the OH number in the case of 1 or 2 NCH₂CH₂OH groups per C(O)CHCHC(O) unit. The imide unit should give 6.5 wt % N and an OH number of 258, whereas the diamide results in 10.1 wt % N and an OH number of 404. The experimental values indicate that the average amount of NCH₂CH₂OH groups per C(O)CHCHC(O) unit is 1.2-1.5. Slightly more than half of the diamide has been converted into the imide.

In the final step, 1 kg of commercially available SMC-B (see Experimental), sawed into pieces of 1 × 3 × 0.4 cm³, was treated with 570 g of EA at 180°C for 48 h. During the reaction, the SMC chips underwent considerable swelling, which did not occur in the case of ethanol, water, or solvents like dimethyl formamide and dimethyl sulfoxide. The reaction mass was poured onto a wide-pore filter to separate the glass fibers. Several washings with methanol and drying *in vacuo* gave 266 g (theoretical, 270 g) of visually clean fibers. Filtration of the heterogeneous remainder gave a gray solid (filler) that was dried and subsequently powdered (441 g; theoretical, 430 g). Distillation of the filtrate at reduced pressure (60 mmHg) as described above resulted in 290 g (theoretical 310 g) of a red-brown solid.

Recycled Materials as Constituents of BMC

The general structure of the polymeric material obtained by solvolysis of SMC, in particular, the presence of hydroxyl groups, invites to crosslinking with

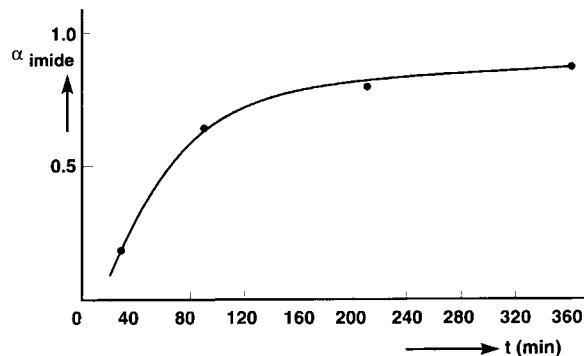


Figure 5 Treatment of *N,N'*-di(2-hydroxyethyl)succinamide at 220°C to give *N*-(2-hydroxyethyl)succinimide and EA.

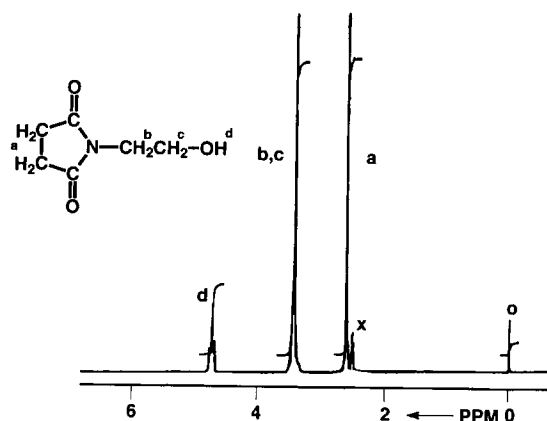


Figure 6 ¹H-NMR spectrum of *N*-(2-hydroxyethyl)succinimide in (x) DMSO-*d*₆. (o) TMS.

epoxy or isocyanate resins. However, the red-brown solid, obtained by solvolysis of SMC-B, appeared to be poorly soluble in these resins, even at temperatures up to 100°C. At this temperature, crosslinking reactions occurred before complete dissolution. The use of a blocked isocyanate did not circumvent this problem. Therefore, we decided not to separate the filler and the organic part. After removal of the glass fibers, the remainder consisting of methanol, ethanolamine, the filler, and the polymer was heated under reduced pressure to distill methanol and ethanolamine. The solid mass was subsequently milled to powder with a diameter less than 0.1 mm.

The effects of adding recycled material to BMC formulations on the mechanical properties of cured sheets were evaluated by comparing various formulations in which the original filler and glass fibers were replaced step by step. According to Table IV, replacing half of the amount of glass fibers by recycled material does not affect the mechanical properties with a possible exception of the Charpy. However, it is difficult to increase the content of recycled glass fibers due to the fact that the volume per weight of these fibers is much larger than that encountered for the virgin materials. The mechanical properties tend to decline upon addition of recycled filler (filler + polymer), which, in particular, occurs when the original filler is completely replaced by recycled filler. This phenomenon is most probably caused by the fact that the content of calcium carbonate decreases. A decreased interaction between filler and the matrix can also be of importance.

CONCLUSION

The polyester-styrene polymer network obtained by curing of SMC can be uncrosslinked in the presence

of ethanol/potassium hydroxide or ethanolamine. The use of the former reagents, however, is restricted to milled SMC, whereas ethanolamine can be used to treat SMC chips, which offers the possibility to recycle the glass fibers. An additional advantage of ethanolamine is that this reagent can be recovered by distillation. The ethanol/potassium hydroxide route results in a large stream of waste chemicals.

Treatment of SMC with ethanolamine affords three fractions, viz., glass fibers, filler, and methanol-soluble polymer containing hydroxyl groups. The polymeric fraction shows little solubility in unsaturated polyester, epoxy, or isocyanate resins.

The recycled glass fibers and the combined filler and polymer can replace half of the virgin fibers and filler of BMC formulations without a serious decline of the mechanical properties.

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