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Analysis of Commercial Unsaturated Polyester Repair Resins

by Kevin Andrews, Scott Bingham, Ian McAninch, Casey Greer, James M. Sands, John J. La Scala, Xing Geng, Giuseppe R. Palmese, Vincent Crisostomo, and Steven Suib

ARL-TR-4872 **July 2009**

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REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
July 2009	Final	1 October 2006–30 September 2008

4. TITLE AND SUBTITLE
Analysis of Commercial Unsaturated Polyester Repair Resins

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Kevin Andrews, Scott Bingham, Ian McAninch,[*] Casey Greer, James M. Sands, John J. La Scala, Xing Geng,[†] Giuseppe R. Palmese,[†] Vincent Crisostomo,[‡] and Steven Suib[‡]

5d. PROJECT NUMBER
EQBRD

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-WMM-C
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-4872

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Environmental Quality Basic Research and Development Program
AMSRD-AAR-AEE-E, Bldg. 355
Picatinny Arsenal, NJ 07806-5000

10. SPONSOR/MONITOR'S ACRONYM(S)
EQBRD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
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14. ABSTRACT
The basic rheological, thermal, and mechanical properties of commercially available repair putties have been determined in this study, as has the composition of these products. These products contain 33% to 40% unsaturated polyester resin, 10% to 20% styrene, and 45% to 57% inorganic fillers. The fillers are made up of hollow glass microspheres, talc, magnesium carbonate, calcium carbonate, fumed silica, glass fibers, and various other minerals. These products have a glass transition temperature of roughly 25 °C and a room temperature storage modulus of 2 to 4.6 GPa. These putties display shear thinning behavior as a result of the fillers. All of these properties provide important benchmark characteristics that must be more or less met by U.S. Army Research Laboratory/Drexel-invented environmentally friendly, hazardous air pollutant–free repair resins utilizing renewable fatty acid-based monomers.

15. SUBJECT TERMS
vinyl ester, styrene, fatty acid monomers, HAP, triglycerides

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					John J. La Scala
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (*Include area code*)
Unclassified	Unclassified	Unclassified	UU	50	410-306-0687

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

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Acknowledgments

The authors thank the Environmental Quality Basic Research and Development Program and the U.S. Army Armament Research, Development, and Engineering Center for funding. This research was supported in part by an appointment of Kevin Andrews and Ian McAninch to the Postgraduate Research Participation Program at the U.S. Army Research Laboratory (ARL) administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and ARL. The authors thank Chief Joanne Wright and the U.S. Army Research, Development, and Engineering Command Reserve Officer Training Corps Cadet Research Internship program for the financial and logistical support of Scott Bingham.

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1. Introduction

Most Department of Defense weapons platforms and support equipment are subject to extremely taxing conditions and are often damaged during weapons fire and off-road operations. For many damage types, small repairs can increase the field life of the platform significantly. Various repair resins, such as Bondo,* Evercoat,† Belzona, 6294 Dent Filler, and 887 Metal-2-Metal Reinforcement, are used in the field-deployed unit and in Army depots, such as Letterkenny Army Depot and Tobyhanna Army Depot (*1*). Repair damage mechanisms for these weapons platforms include impact from foreign object damage, ballistic impact, moisture intrusion and expansion, corrosion, collision, and maintenance-induced damage (*2, 3*). Damage levels are categorized as follows:

- Light – aesthetic repairs and coating repairs.
- Moderate – delaminations, small patches, and edge repairs.
- Heavy – full depth, core, and substructure repairs.

Other criteria for selecting the appropriate repair include whether the component can be removed and whether the back side is accessible. For a typical moderate field repair, any remaining coating in the repair area is removed by hand sanding or portable tools. Damage is cut out in an appropriate configuration, often circular. Scarfing, removing top layers of material done at a shallow angle, is commonly done by hand. The surface is then sanded further and cleaned using an available solvent. Composite repair resins, such as Bondo, containing short reinforcing fibers can then be applied to the damage zone. The resin cures at room temperature. Light repairs will be done similarly using Bondo and similar composite repair resins without much, if any, scarfing. Depot repair is typically a bit more elaborate. Rather than using simple repair resins for moderate or heavy damage, the damage zone will be filled with fibers or honeycomb and vacuum infused or cured using wet layup (*2, 3*). This allows the use of more elaborate resin systems, such as phenolics, and autoclave cure. However, for most light repair and some moderate repair, Bondo and similar resins will be used. Not only are these repair resins used in composite structures, they are also used to do light and moderate repair of non-armor metal structures, such as body paneling, by filling in holes and dents in a manner similar to that used for composite structures (*4*).

A recent report to the Army states that there are no environmentally friendly repair resins (*5*). Repair resins contain ~20 weight-percent (wt%) styrene or other hazardous air pollutants (HAPs), which is up to 50% of the resin content (*6, 7*). These HAP chemicals are used to reduce

*Bondo is a registered trademark of Bondo Corporation.

†Evercoat is a registered trademark of Fibre Glass-Evercoat.

repair resin viscosity to make it easy to blend and easy to apply. Furthermore, recent work has shown that HAP emission from vehicle repair is one of the largest sources of emissions from miscellaneous coatings in the Army (*1*). Field repair resins are always cured in the open, and it is impractical to use enclosures and trapping devices, such as scrubbers, to remove and recover these HAP emissions.

Through implementation of the Clean Air Act, the Environmental Protection Agency has established regulations limiting the amount of HAPs that can be used in composite materials, including repair resins (*8*). This new regulation proposes facility-wide emissions limits through the National Emissions Standards for Hazardous Air Pollutants, which makes compliance through low emissions materials necessary (*8*). One aspect of this law requires continuous emissions monitoring of all HAP-containing composite materials. Therefore, this legislation will have a significant impact on the military's use of composite materials, as well as commercial applications, unless methods for mitigating HAP emissions during processing of composite parts are developed. Furthermore, the high reactivity of repair chemistry results in current technology with a short shelf life (<1 year) (*9*). Thermal and mechanical performance characteristics decrease rapidly after the shelf life (*9*). Consequently, the military generates thousands of pounds of hazardous waste from expired resins annually (*4*, *9*).

The U.S. Army Research Laboratory (ARL)/Drexel University have recently shown that methacrylated fatty acid monomers are ideal candidates to replace styrene in vinyl ester (VE) and unsaturated polyester (UPE) resins because they are inexpensive, have low volatilities, and promote global sustainability because they are derived from renewable resources (*10–12*). The resulting fatty acid VE/UPE resins and composites have similar properties relative to commercial resins while having better dimensional stability, lower exotherm, higher toughness, and lower emissions (*10*). Fatty acid monomers could therefore reduce or eliminate HAP emissions in repair resins. In order to evaluate fatty acid-based repair resins, the benchmark thermal, mechanical, and chemical properties of commercial repair resins must be obtained. Therefore, this work presents an analysis of various commercial Bondo and Evercoat repair products. In particular, this work examines the composition of commercial repair putties as well as a survey of their rheological, thermal, and mechanical properties.

2. Literature Findings of Repair Resins

Repair resins are usually two-part formulations composed of a number of different components (figure 1) (*6*, *7*, *13–21*). The putty component, referred to as "part A" in this work, contains the polymeric binder components, including a cross-linking agent (VE or UPE monomers), a reactive diluent, such as styrene, a free-radical decomposition promoter, free-radical inhibitors, and various inorganic additives, such as talc, magnesium carbonate, chopped glass fiber, and fumed silica.

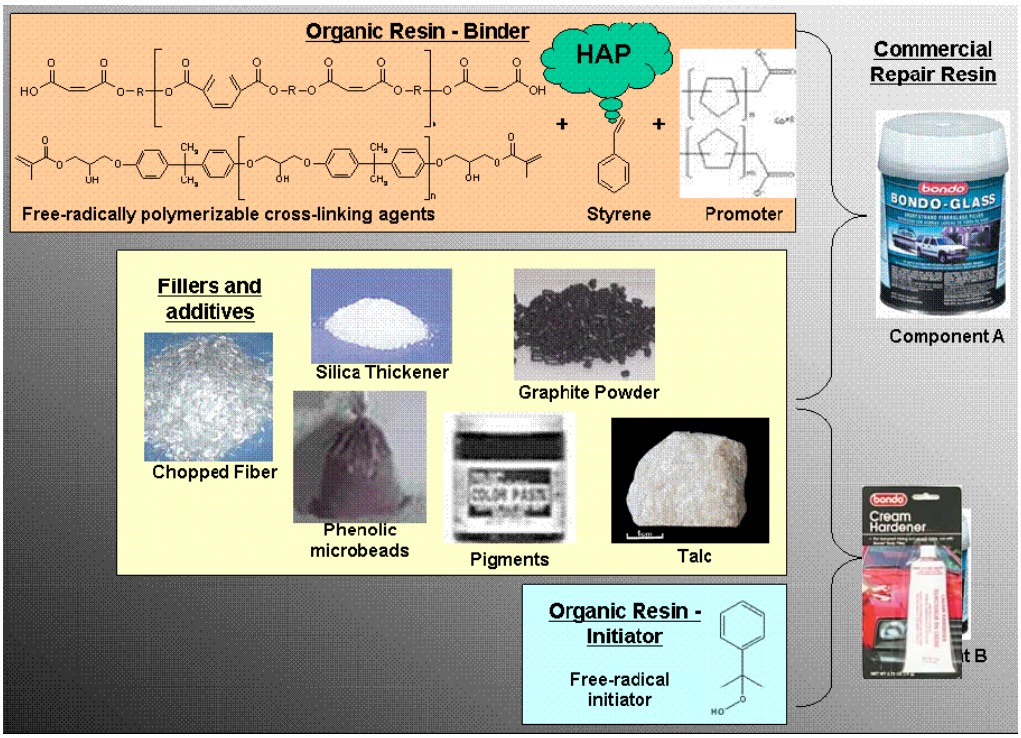

Figure 1. Various organic and inorganic components are used in commercial repair resins, such as Bondo.

Part B contains the free-radical initiator and surfactants to enable successful mixing of this hardener into viscous part A. Part B usually consists of only a small fraction of the total repair resin mass (1 to 5 wt%).

Five types of Bondo were used in this work:

- Prod. no. 272 - Bondo Glass (BG)
- Prod. no. 262 - Bondo Body Filler (BBF)
- Prod. no. 20052 - Bondo All-Purpose Putty (BAP)
- Prod. no. 2682 - Bondo Boatyard Resin (BBR)
- Prod. no. 402 - Bondo Fiberglass Resin (BFR)

Four types of Evercoat were used in this work:

- Prod. no. 100639 - Evercoat Glass Lite Filler (EG)
- Prod. no. 100151 - Evercoat Lite Weight High Production Filler (EBF)
- Prod. no. 100106 - Evercoat RAGE – Premium Liteweight Filler (ERAGE)
- Prod. no. 100416 - Evercoat Metal Glaze (EMG)

Hexion 713-6150 (HEX) is known to be the base resin for preparing Bondo putties* and was used and analyzed in various aspects of this work.

The material safety data sheets (MSDSs) give quite a bit of information of the contents of these repair resins (*6*, *7*, *13–20*). Other literature searches revealed little about the composition, properties, or even use of repair resins. Tables 1 and 2 list the chemical makeup of these resins according to the MSDS and product literature (*6*, *7*, *13–21*). The full composition of BG was not found; it should be similar to the other Bondo resins but with short glass fibers and without any sodium metaborate. The UPE component is listed as a diethylene glycol (DEG), maleic anhydride, phthalic anhydride copolymer. Talc is a typical low-weight filler used in polymer composites to help impart dimensional stability and rigidity (*22*). Magnesium compounds ionically interact with the carboxylic acid groups in UPE to increase the resin viscosity at low temperature and low shear (*23*). However, the addition of heat or shear breaks up the bonds to reduce the viscosity.

Table 1. The contents of Bondo repair products according to product MSDS (*6*, *7*, *13–20*).

Component	**BG (wt%)**	**BBF (wt%)**	**BAP (wt%)**	**BBR (wt%)**	**BFR (wt%)**
UPE	—	30–40	30–40	60–70	60–70
Styrene	15–20	10–20	10–20	30–40	30–40
Talc	—	20–30	20–30	0	0
Magnesium carbonate	—	10–20	10–20	0	0
Sodium metaborate	0	5–10	5–10	0	0
Fibrous glass	1–10	0	0	0	0

Table 2. The contents of Evercoat repair products according to product MSDS (*6*, *7*, *13–20*).

Component	**EG (wt%)**	**EBF (wt%)**	**ERAGE (wt%)**	**EMG (wt%)**
UPE	25–30	30–35	30–35	30–35
Styrene	15–20	15–20	15–20	20–25
Talc	40–45	30–35	25–30	10–15
Magnesium carbonate	10–15	5–10	5–10	—
Calcium carbonate	—	5–10	10–15	10–15
Titanium dioxide	—	—	0–1	1–5
Quartz (crystalline silica)	—	—	0–2	—
Fibrous glass	[a]	—	—	—
Inert filler (proprietary)	1–5	1–5	1–5	5–10

[a]Although fibrous glass is not listed as a component on the MSDS of EG, the repair putty contains fibrous glass.

*According to personal correspondence with Hexion Corp.

The B component for Bondo, the Red Cream Hardener (RCH), is a benzoyl peroxide-based initiator. Benzoyl peroxide is a frequently used free-radical initiator (*22*). The components and contents for the cream hardeners are listed in table 3 according to the MSDS (*16*, *21*). The alkyl benzoate and non-phthalate plasticizer are oily chemicals added to allow the easy dispersion of hardener throughout component A. Zinc stearate is a surfactant added to emulsify the water-oil mixture. The hardener used with the Evercoat utilizes a similar benzoyl peroxide-based product for use with its repair resins.

Table 3. The contents of Bondo and Evercoat cream hardeners according to product MSDS (*16*, *21*).

Component	**Content (wt%)**	
	Bondo RCH	**Evercoat Hardener**
Benzoyl peroxide	40–50	45–50
Water	10–20	15–20
C9–C11 branched alkyl benzoate	10–20	—
Zinc stearate	1–5	—
Other	>5%	—
Plasticizer, non-phthalate	—	25–30
Silica, amorphous	—	0–2
Calcium carbonate	—	0–2
Pigments	—	0–2

3. Experimental Procedure

The following experiments were performed to more accurately determine the composition of commercial repair resins. In addition, the performance of repair resins was characterized and presented to benchmark the required performance of alternative formulations.

3.1 Component Separation

Roughly 15 g each of BG, BBF, BAP, EG, EBF, ERAGE, and EMG were dissolved in 25 g of acetone to separate the organic and inorganic components. The organic components dissolved in the acetone phase, whereas the insoluble inorganic components split into two solid phases: one phase that was less dense than the organic liquid phase and one phase that was more dense. Centrifugation at 10,000 rpm for 10 min was used to increase the rate of separation of the inorganic components. As shown in figure 2, the samples separated into three phases: (1) insoluble inorganics less dense than the liquid organic phase (referred hereafter as the “foam” layer) (top of tube in figure 2), (2) the liquid organic phase (with the acetone), and (3) insoluble inorganics denser than the liquid phase (bottom of tube in figure 2). The foam and organic layer

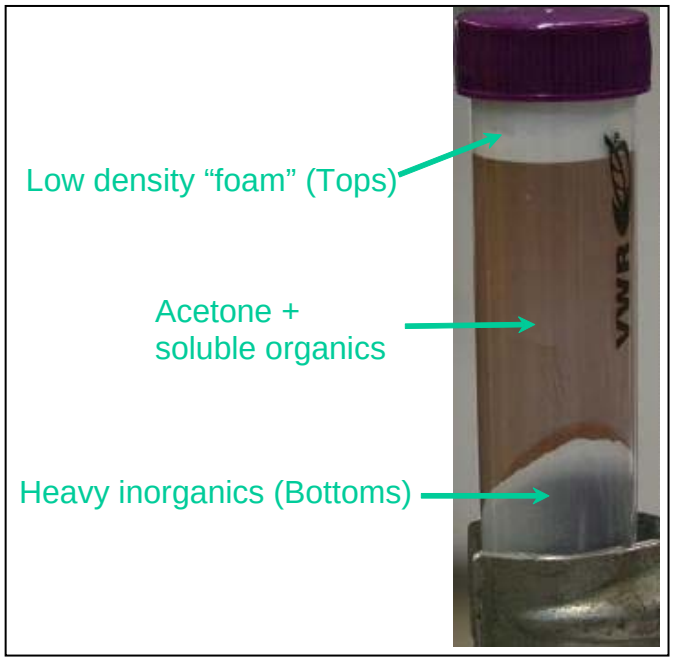

Figure 2. Photograph showing the three distinct layers produced during component separation of BBF in acetone in a 50-mL centrifuge tube after centrifugation at 10,000 rpm for 10 min.

were carefully decanted into an Erlenmeyer flask through a Büchner funnel fitted with Whatman no. 2 filter paper (Whatman International Ltd, England). Twenty-five additional grams of acetone were added to the centrifuge tube to extract residual organics from the heavy inorganics, and the tube was respun and decanted into the same flask (3×). Both inorganic layers were allowed to dry in opened containers for 3 days and then weighed. The volatiles from the organic layer (consisting of the acetone used in the extraction and styrene that is part of these repair products) were removed by allowing the resin to evaporate in a fume hood for 3 days and then storing at 50 °C and 30–31 inHg vacuum for 1 week. The weight fractions of the foam and heavy inorganics were calculated by dividing the weight of the respective phase by the initial weight of repair resin used in the extraction. Once the bulk of the styrene and acetone was removed (as confirmed by nuclear magnetic resonance [NMR]), the organic phase, which was almost pure UPE, was weighed and the UPE fraction of the repair resin was taken to be the weight of this phase divided by the initial repair resin weight. The styrene that had been present in the initial repair resin weight used in the extraction had evaporated, so the difference between unity and the sum of the three phases (foam, heavy inorganics, and UPE) was taken to be the styrene weight content of the repair resin.

3.2 Promoter Analysis

Chemically or physically determining the promoter content in resins is quite difficult considering the very low concentration in which they are used (<1%). Therefore, commercially available promoters were added to a VE resin, which is very similar to polyester resin, and were cured

with Bondo RCH. Formulations that do not cure will indicate which promoters are not compatible with RCH. Cobalt naphthenate (CoNap), N,N-dimethylaniline, and mixtures of CoNap and N,N-dimethylaniline were used. A similar analysis for the Evercoat blue cream hardener and Evercoat UPEs was not performed.

3.3 Nuclear Magnetic Resonance Spectroscopy

NMR samples were prepared by dissolving the A components of each Bondo and Evercoat product component in deuterated chloroform (99.8 atom-percent, Fisher Scientific). The inorganic component settled out or was forced to settle out of the solution using centrifugation. Samples were prepared at concentrations of ~25 mg/mL in deuterated chloroform. A Bruker 600-MHz spectrometer with a spectral window of ±4800 Hz, 16 scans at 293 K, and 90° pulse width was used.

The NMR spectra for UPE monomers are well characterized (*24*). Typical UPE components used are shown in figure 3. Figure 4 shows an example NMR spectrum of a typical DEG polyester with phthalic acid (PA), fumaric acid (FA), and maleic acid (MA) (*24*). DEG peaks appear at 4.4 and 3.7 ppm, each representing four protons. The PA peaks appear from 7.4–7.8 ppm and represent the four phthalic anhydride aromatic protons. The two protons attached to the unsaturation sites of FA and MA appear at 6.9 and 6.3 ppm, respectively. The 12 protons of suberic acid (SA) produce peaks at 1.3 and 0.85 ppm. The molar concentrations of each component were determined by measuring the area of the peaks and dividing by the number of protons responsible for each peak. Ethylene glycol (Egly) is also commonly found in UPE resins and its four methylene protons produce a single peak at 4.6 ppm (*24*). Terephthalic acid (TP) is also used to stiffen the UPE (*25–27*), and its four aromatic protons produce a single peak at 7.9 ppm (*24*). The molar ratios of the UPE component of the resin were calculated by integrating the peak areas of interest and dividing the areas based on the number of protons that create the peak, and, if when this was done for all of the UPE components, the UPE composition was determined.

The NMR spectra were also analyzed to determine the styrene content in the organic resin component of the repair resin. The five aromatic protons on styrene appear at 7.25–7.5 ppm (*28*). The vinyl CH proton appears at 6.75 ppm, and the vinyl CH_2 protons appear at 5.78 and 5.28 ppm.

To obtain a 95% confidence interval for the calculated UPE constituents, NMR was performed 11 times for BBF, and the variance in the calculated values was used to determine the error.

3.4 Size Exclusion Chromatography

Size exclusion chromatography (SEC) was run to measure the molecular weight of the UPE resins. A Waters 515 gel permeation chromatograph was used with two 5-µm styrene-divinyl benzene columns in series. The columns were equilibrated and run at 45 °C using

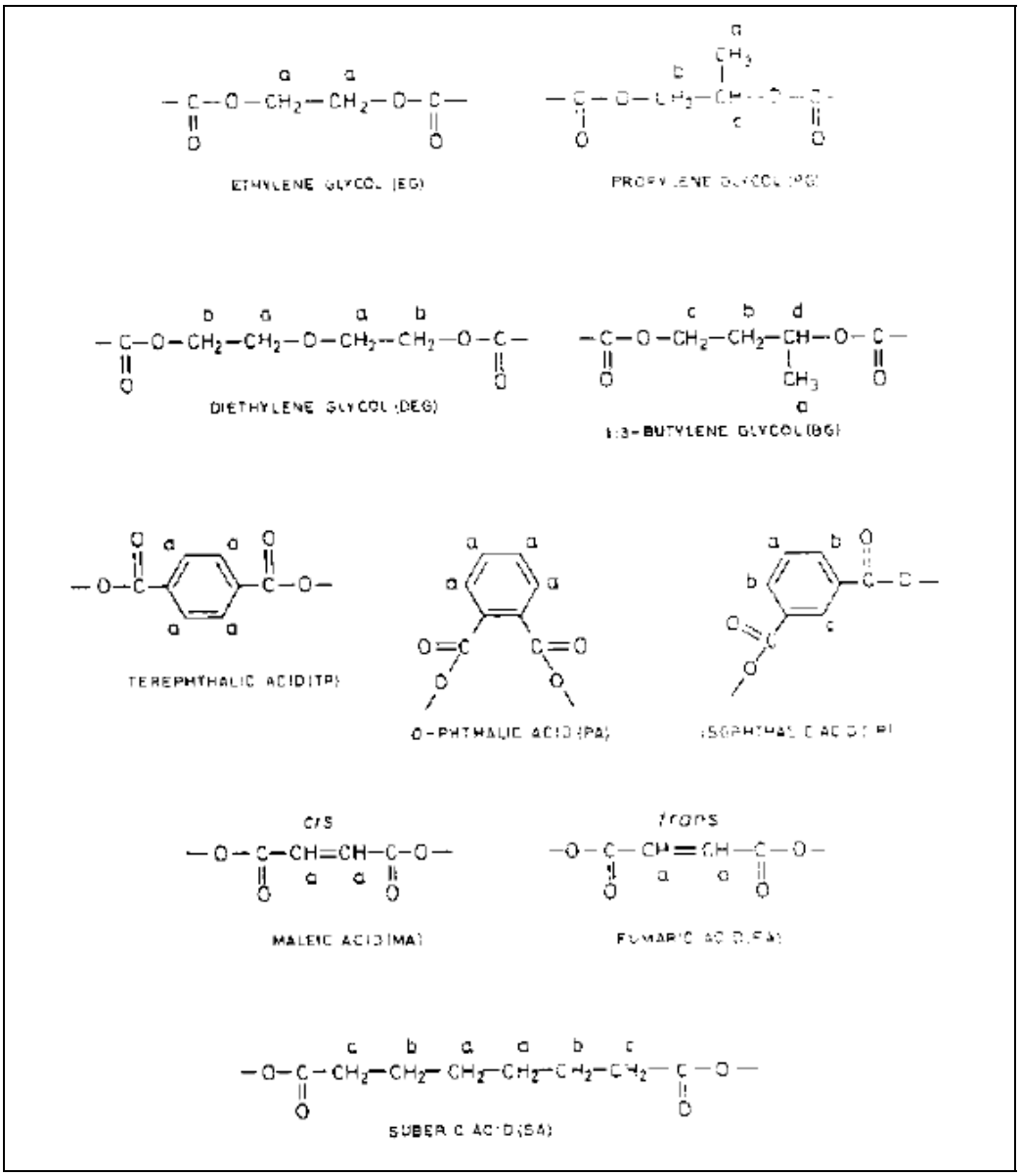

Figure 3. Typical components of UPE monomers. (Figure reproduced from Haslam et al. [*24*].)

tetrahydrofuran (THF, Aldrich, Milwaukee, WI) as the elution solvent at a flow rate of 1 mL/min. The column effluent was monitored by two detectors operating at 25 °C: a Waters 2410 refractive index detector and a Waters 2487 dual absorbance detector operating at 270 and 254 nm (absorbed by phenyl rings). Samples were prepared by dissolving a 2-mg sample in 1 mL of THF. Because high molecular weight species cannot diffuse into the pores of the packing, they elute first from the column, while lower molecular weight species elute later (*29*).

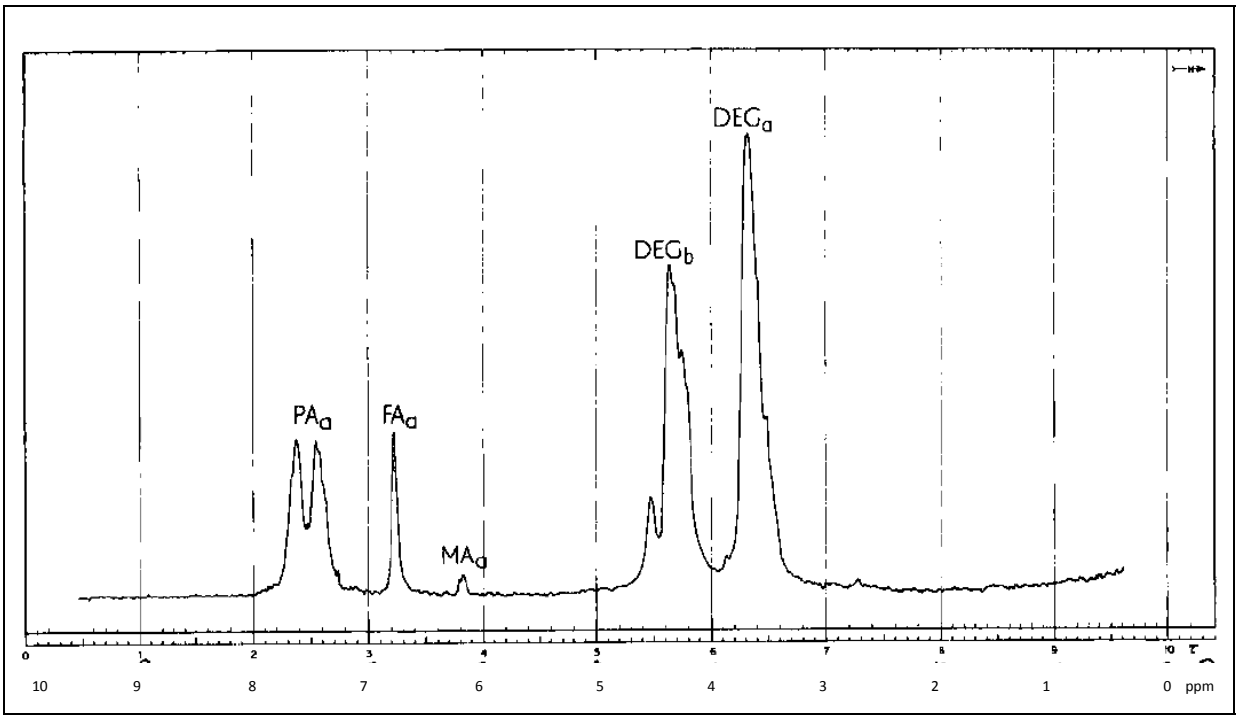

Figure 4. NMR spectrum of UPE based on DEG, PA, FA, and MA. Peak assignments correspond to the molecular structures in figure 3. (Figure reproduced from Haslam et al. [*24*].)

Standards with known molecular weights were used to calibrate the molecular weight (*30*). The standards used were styrene (MW = 104 g/mol), VE 825 (MW = 514 g/mol), Epon 1001F (MW = 340 g/mol, 624 g/mol, and 0.1400 g/mol), Epon 1004F (MW = 340, 624, and 1950 g/mol), Epon 1007F (MW = 3940 g/mol), Epon 1009F (MW = 5548 g/mol), and several higher molecular weight polystyrene standards (MW = 22k, 66k, 127k, 220k, and 770k). Epon 1001F and 1004F have multiple peaks because they are a combination of bisphenol A epoxy monomers with different degrees of polymerization.

The molecular weight calibration is good (figure 5) and is described by the following equations:

$$MW(t) = \begin{cases} 7.13*10^{12}*\exp(-1.73*t), & t \le 13.12 \\ 4.51*10^{5}*\exp(-0.467*t), & t > 13.12 \end{cases}, \quad (1)$$

where t is the SEC retention time (in minutes). A transition occurs at about 13.1 min, which necessitates the need for two fitted equations to describe MW(*t*).

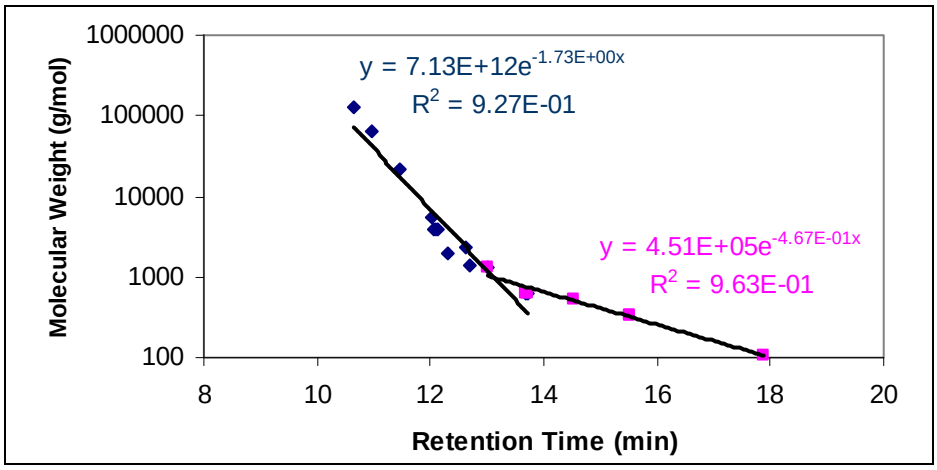

Figure 5. The calibration of molecular weight vs. retention time.

The time scale of the repair resin UPE absorption spectra was shifted so that the styrene peak was centered at 18 min retention time, and the baseline for the peaks of interest were taken as a line connecting the minima between peaks, as shown in figure 6. In the event of bimodal UPE peaks, the peaks were treated as a single entity. During a single run, by assuming that the molar absorptivity at a given frequency is a function only of the product of the molecular weight and the molarity at any time, the number average molecular weight is calculated as follows (*31*):

$$M_n = \frac{\sum H(t_i)\Delta t_i}{\sum \left[\frac{H(t_i)\Delta t_i}{MW(t_i)} \right]} , \qquad (2)$$

where $MW(t_i)$ is the molecular weight at time t_i (from equation 1), $H(t_i)$ is the peak height (absorbance with baseline correction) at t_i, and Δt_i is the duration since the last reading (e.g., $t_i - t_{i-1}$). The sum is taken over the domain of the UPE peak, and the absorption at 254 nm was used.

3.5 Optical Microscopy Characterization

The inorganic components (figure 2, bottoms) recovered from the Bondo and Evercoat separation step were analyzed using optical microscopy. First, the solvents were removed by drying the samples in the fume hood until the sample mass no longer decreased with time, which usually required 3 days. An Olympus MX50 microscope in darkfield imaging mode with 10×, 20×, and 50× objectives were used to view the samples. Commercially available inorganic fillers, including glass microspheres, talc, magnesium carbonate, and milled fiberglass, were also analyzed using optical microscopy in an attempt to identify the inorganic components.

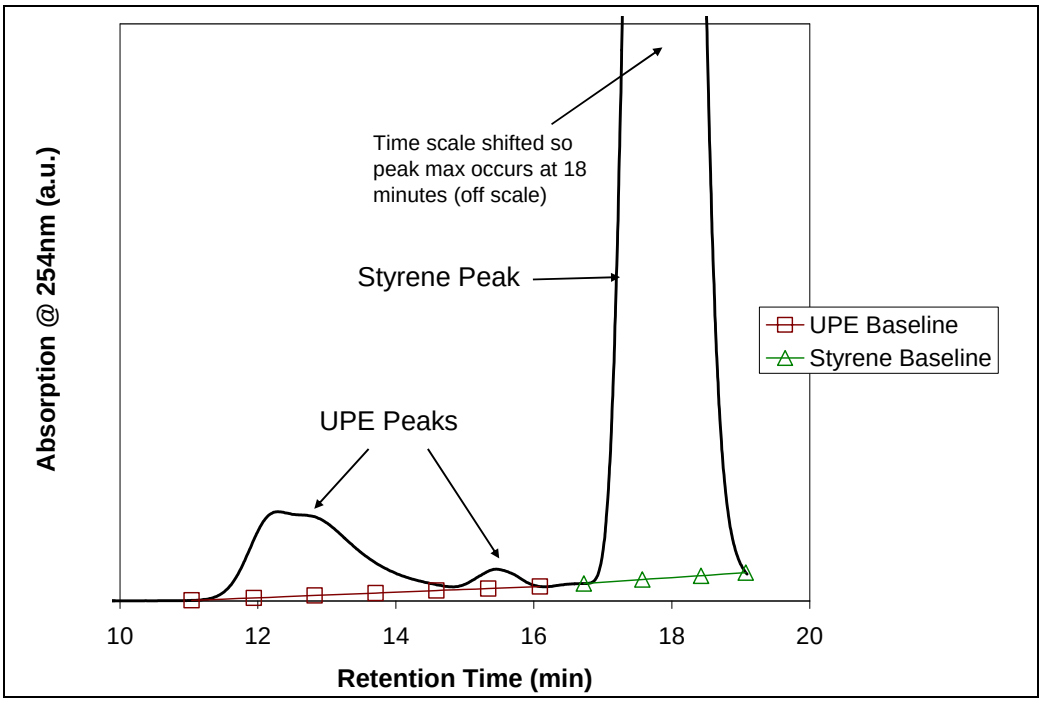

Figure 6. Typical SEC absorption time series at 254 nm for a UPE in styrene (Evercoat RAGE).

3.6 X-ray Fluorescence (XRF) Analysis of Inorganic Particulate Fillers

The extracted inorganic particulates from the component separation were analyzed using a Philips 2404 WDXRF spectrometer to collect the x-ray intensities from all the elements between sodium and uranium. Uniquant software was used to calculate the concentrations from the measured x-ray intensities. Elemental concentrations are summed and normalized to 100%. The sodium concentrations may be slightly inaccurate due to adsorption by the polypropylene window used as part of the sample holder, although the software should correct for this. However, significant amounts of sodium-containing fillers should not be present in the formulations, so the effect of any inaccuracy in the sodium signal will be minimal.

3.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was run on the Bondo and Evercoat products using a TA Instruments Hi-Res TGA 2950. A 10- to 15-mg sample was placed on a platinum sample holder. The samples were run in air up to 800 °C at 10 °C/min. The instrument measures the sample mass as a function of temperature throughout the experiment. Liquid component A samples and liquid cream hardener (component B) were run. In addition, cured samples for the three types of Bondo repair resins were also run.

3.8 Rheology and Viscosity Characterization

The viscosities of the liquid samples were measured using a TA Instruments (New Castle, DE) AR2000 Rheometer in steady shear flow experiments using parallel plate geometry (40-mm plates). The shear rate was increased from 0.001 to 10 s^{-1} and then decreased back to 0.001 s^{-1},

and 5 or 10 measurements were taken per decade. At a given shear rate, the shear stress was measured every 2 s. The shear rate and viscosity were recorded when the shear rate stabilized to within 5% tolerance for three consecutive intervals.

3.9 Dynamic Mechanical Analysis

The thermomechanical properties of the repair resins were measured using dynamic mechanical analysis (DMA). Samples were prepared by mixing 15 to 20 g of resin with 2 wt% RCH or Blue Cream Hardener (BCH) in disposable polypropylene beakers. After thorough manual mixing, duplicate samples were poured into two negative molds to produce a rough rectangular shape. After curing at room temperature for 2–3 days, the samples were removed from the mold and sanded with 150-grit sandpaper to rectangular dimensions with tolerances of ±0.05 mm on each side. Rectangular samples with approximate dimensions of 60 × 12 × 3.5 mm were tested using a TA Instruments 2980 DMA in dual cantilever geometry. The samples were tested at 1 Hz with a deflection of 15 or 7.5 μm while ramping the temperature from –50 °C to 150 °C at a rate of 2 °C/min. Two temperature ramp experiments were run for each sample. The two runs were nearly identical, indicating almost complete cure before the first run and indicating that additional DMA ramps were unnecessary.

The temperature at which the peak in the loss modulus occurred in the fully post-cured polymer was considered the glass transition temperature (T_g) of the material (*6*). The experimental error in T_g was ±1 °C. Tan delta can also be used as a measure of T_g, but it is known that the maximum in tan delta is 10–20 °C above the T_g (*32*).

3.10 Flexural Testing

Samples were prepared by mixing 50 g of resin with 2 wt% RCH or BCH in disposable polypropylene beakers. The samples were poured into rectangular molds and cured at room temperature for 3 days. The samples were then cut into rectangular samples and sanded to have nominal dimensions of 10 × 80 × 64 mm. Flexural tests, in accordance with ASTM 790 M (*33*), were performed to determine the modulus of elasticity and flexural strength. The samples were tested flat-wise on a support span, resulting in a support-to-depth ratio of 16. All tests were performed at ambient conditions, which were ~22 °C and 40% relative humidity. The samples were tested using an Instron at a crosshead speed of 10 mm/min. The flexural modulus, elongation at failure, and flexural strength were calculated according to the ASTM standard.

4. Results and Discussion

4.1 Component Separation Results

The final mass of the organic and inorganic components was measured to determine the mass percent of each component (table 4). All of the products fall within fairly tight guidelines:

Table 4. Organic, inorganic, and foam composition of Bondo and Evercoat putties as determined experimentally through mass measurement of solvent-extracted samples.

Type	UPE (wt%)	Styrene (wt%)	Inorganic (wt%)	Foam (wt%)
BG	32.9	10.3	56.8	0
BBF	37.5	9.7	47.0	5.7
BAP	39.9	13.7	42.0	4.5
EG	29.9	13.2	56.0	0.8
EBF	34.6	15.7	44.7	5.0
ERAGE	34.9	13.3	48.4	3.5
EMG	36.3[a]	20.2[a]	35.9	7.6

[a]The sum of the UPE and styrene was determined by component separation, but NMR was used to determine that the ratio of UPE to styrene is 1.79.

30 to 36 wt% UPE, with 10 to 20 wt% styrene, 36–56 wt% inorganic particulates, and 0–8 wt% "foam." Perhaps surprisingly, more than half of the repair putty mass consists of inorganic particulates or filterable lightweight fillers (the "foam") for all putties except EMG.

4.2 Promoter Analysis

VE resin did not cure when promoted with CoNap using the RCH initiator, which is known to be a benzoyl peroxide initiator (*16*). However, samples promoted with N,N-dimethylaniline cured at rates directly proportional to the promoter concentration. Mixtures of N,N-dimethylaniline and cobalt naphthenate also cured the VE resin. However, the rate was only dependant on the N,N-dimethylaniline concentration. The polyesters used in this work all came prepromoted. Additional CoNap did not affect the cure speed or gel time, while additional N,N-dimethylaniline decreased the gel time proportionally. Thus, CoNap is not used to promote the cure of the UPE repair resins, while N,N-dimethylaniline is likely the promoter used.

4.3 Nuclear Magnetic Resonance Spectroscopy Results

The mole-percent styrene and UPE can easily be calculated using the NMR spectra through the ratios of polyester and styrene peaks divided by their respective proton areas (table 5). The weight-percent of the components was calculated by factoring in the molecular weights of the various monomer components of UPE and styrene. Table 5 shows the composition of the UPE resins, including the amount of styrene, and figure 7 shows a representative NMR spectrum.

UPEs are typically composed from the condensation reaction of dialcohols and diacids (*24, 26*). Overall, Bondo and Evercoat UPE repair putties can be regarded as a DEG, PA, FA copolymer with small amounts of Egyl, glycol, other diol, MA, and SA in some formulations. By replacing part of the PA content with TP, the strength, heat resistance, flexibility, and toughness should be increased (*26, 27*). Increasing the amount of FA and MA—the only UPE components to contain ethylenic bonds capable of copolymerizing with styrene—will increase the extent of crosslinking. SA's six-carbon alkyne segment will likely increase flexibility and lower the T_g of the resulting polymer. Increasing the styrene content will increase the T_g and rigidity of the resulting thermoset.

Table 5. The composition of Bondo UPE resins.

Resin	Styrene Content (wt%)	UPE Composition (mol %)								
		DEG	EGly	Glycol (2.5 Carbon)	Other Alcohol	PA	FA	MA	SA	TP
Molecular weight of constituents UPE (g/mol)->		72.1	28.1	28.1	28.1	164.1	114.0	114.0	172.2	164.1
HEX	24	50	—	—	—	39	9	1.0	1.1	—
BG	24	50	—	—	—	39	9	0.6	1.1	—
BBF	22	50	—	—	—	39	9	1.3	1.2	—
BAP	23	50	—	—	—	38	10	1.1	1.7	—
BBR	28	28	16	1.3	4.7	12	15	2.6	—	21
BFR	28	31	14	1.7	3.8	13	15	1.8	—	21
EG	27	50	—	—	—	32	10	0.8	7.3	—
EBF	25	50	—	—	—	35	10	1.3	4.5	—
ERAGE	25	50	—	—	—	31	9	1.1	9.2	—
EMG	36	50	—	—	—	32	10	1.1	6.6	—
±	3	1	2	0.2	0.4	2	1	0.3	0.6	1

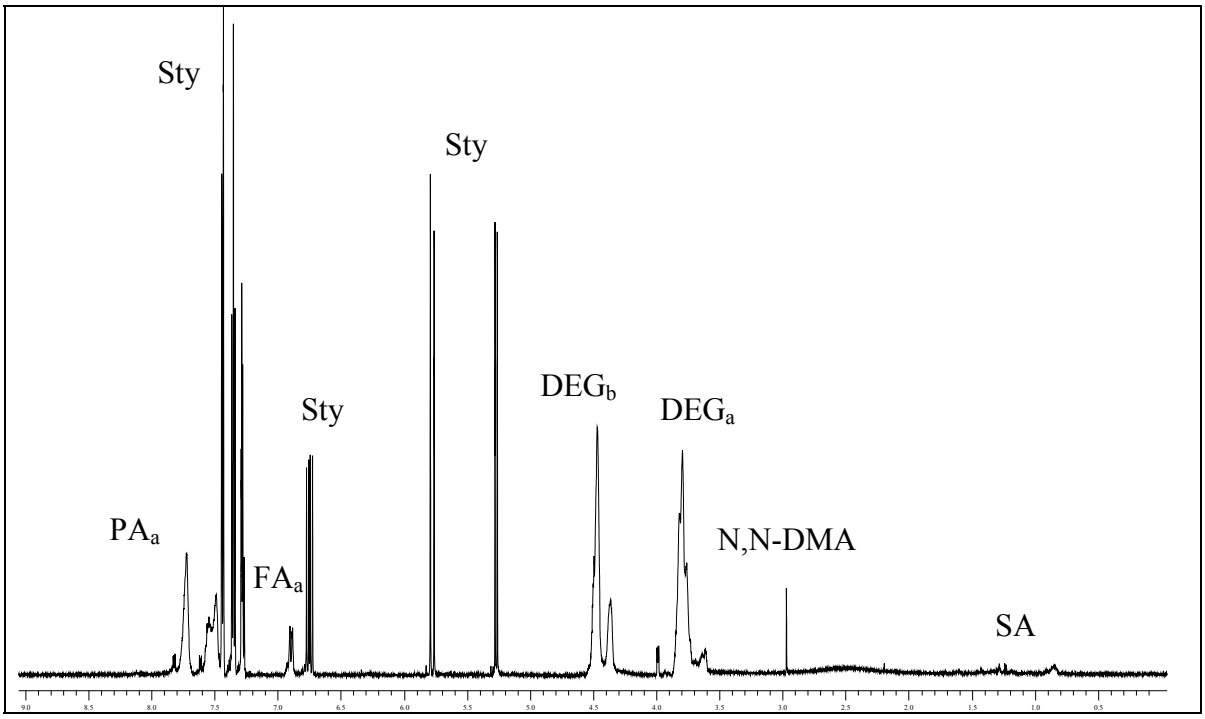

Figure 7. NMR spectrum of BG UPE and styrene. Peak assignments correspond to the molecular structures in figure 2.

An analysis of the NMR spectra of the UPEs shows that the repair products' resins may be grouped as follows:

- Group 1: HEX, BG, BBF, and BAP
- Group 2: BBR and BFR
- Group 3: EG, EBF, and ERAGE
- Group 4: EMG

According to NMR analysis, resins within the same group appear to be the same organic resin. Resins in different groups have significant differences between their UPE-to-styrene ratio or UPE chemical makeup.

HEX, BG, BBF, and BAP all contain roughly 23 wt% styrene and utilize DEG as the only diol and rely heavily on PA for a diacids. BBR and BFR use a mixture of alcohols, use TP, have more reactive vinyl bonds, and have higher styrene contents, all of which will produce a higher T_g and a more heavily crosslinked, cured polyester. Evercoat products contain slightly more styrene than their Bondo counterparts (EG-BG, EBF-BBF, and ERAGE-BAP) and also contain much more SA. EMG had the most styrene at 38% of the resin mass.

BBR and BFR were chemically different from BG, BBF, and BAP (table 5). DEG, MA, FA, and styrene appeared in the same locations as they did for BG, BBF, and BAP. Additional peaks appeared in BBR and BFR: TP appears at 8.1 ppm, EG appears at 4.5 ppm, other glycols with an average of 2.5 carbon atoms appear at 5.5 ppm, and other alcohols appear at 2.9–3.5 ppm (figure 8). Both BBR and BFR had 28 wt% styrene. Overall, the NMR spectra of BBR and BFR were identical, indicating they are the same UPE with the same styrene content.

Figure 9 shows the NMR spectrum of N,N-dimethylaniline. The peaks at 7.3 and 6.8 ppm represent its aromatic protons, and these peaks are coincident with the styrene peak. The N,N-dimethylaniline peak at 2.90 ppm represents the six methyl protons and does not overlap with any other UPE or styrene peaks. This peak is evident in the NMR spectra of all Bondo (figure 7) and Evercoat putties and resins. Considering these results and the cure results, N,N-dimethylaniline is very likely to be the promoter for Bondo and Evercoat.

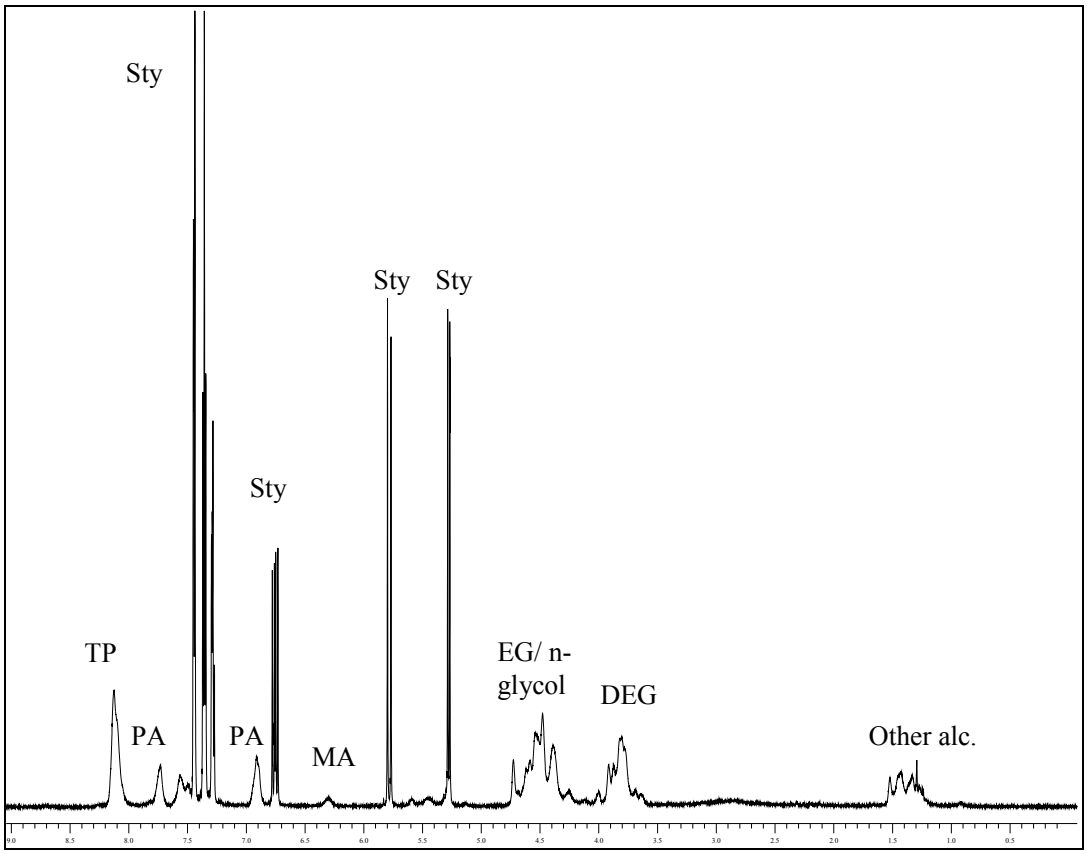

Figure 8. NMR spectrum of Bondo BBR.

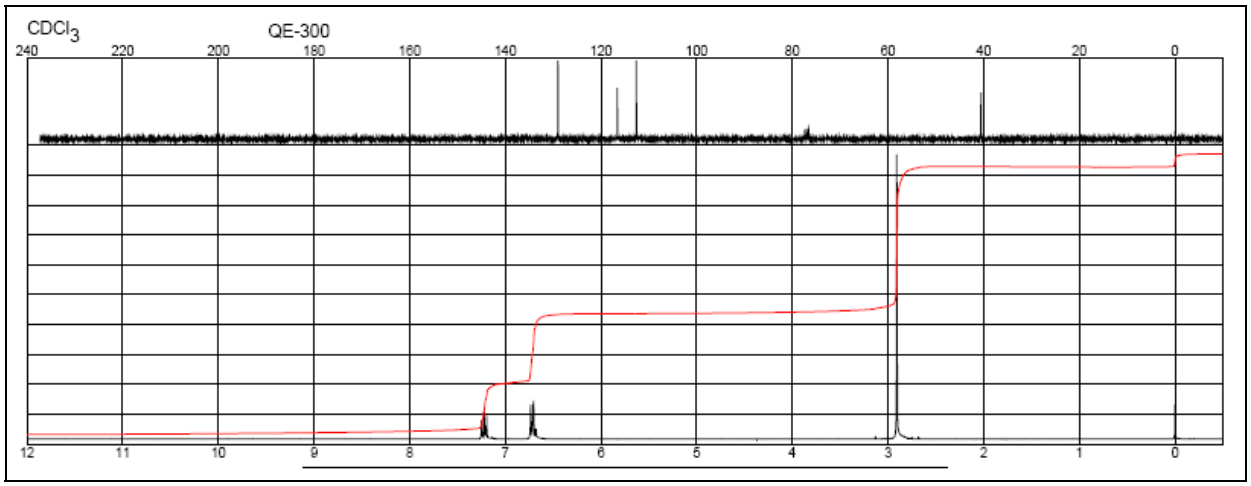

Figure 9. NMR spectrum of N,N-dimethylaniline (*34*).

4.4 Size Exclusion Chromatography Results

SEC showed that the commercial repair resins had multiple peaks (figure 6). The peak at ~18 min represents styrene. The multiple peaks ranging from 10 to 17 min represent the UPE monomers. The broadness of the peak indicates that there is a large distribution of molecular weights that make up this monomer. The molecular weights of the UPE monomers, $MW_{av\ i}^{UPE}$, were calculated using equation 2 and are shown in table 6. The molecular weights are probably accurate to within ±100 g/mol. The UPE molecular weights range from 947 to 1352 g/mol.

Table 6. The molecular weights of the UPE components of Bondo repair resins and the corresponding number of polymerizable double bonds per UPE monomer.

Product	M_N (g/mol)	No. Vinyl per Molecule	MW of UPE Monomer for Two Vinyl Groups
HEX	1088	1.0	2254
BG	1000	0.9	2272
BBF	990	0.9	2209
BAP	980	0.9	2114
BBR	1030	1.8	1159
BFR	1020	1.8	1239
EG	—	—	2183
EBF	1352	1.3	2084
ERAGE	1207	1.0	2322
EMG	947	0.9	2026
±	131	0.39	100–400

Only FA and MA have polymerizable ethylenic unsaturation, so these constituents are crucial to the crosslink density of the cured network. The mole-percent vinyl groups per UPE based on the NMR results are shown in table 5. Based on this and the molecular weight of the UPE components (table 5), the average molecular weight of a monomer repeat unit for the UPE is:

$$MW_{repeat}^{UPE} = \sum MW_i \cdot x_i \ , \tag{3}$$

where MW_i is the molecular weight of the ith diol or diacid and x_i is the mole fraction of the diol or diacids. The summation is performed over all of the diols and diacids present in the UPE. The number of vinyl group per UPE monomer, N_{vinyl}^{UPE}, can then be calculated:

$$N_{vinyl}^{UPE} = \frac{(x_{FA} + x_{MA}) MW_{av}^{UPE}}{MW_{repeat}^{UPE}} \ . \tag{4}$$

FA and MA refer to the vinyl units of fumaric acid and maleic acid, respectively. Free-radical crosslinker molecules must have two or more polymerizable unsaturation sites per molecule (*35*). The theoretical molecular weight to obtain two crosslinkable vinyl bonds per UPE monomer may be obtained from the following equation:

$$MW_{2vinyl}^{UPE} = \frac{2MW_{av}^{UPE}}{N_{vinyl}^{UPE}} \quad . \tag{5}$$

The results (table 6) show that the molecular weights of the UPE monomers are generally significantly lower than expected based on an average of two cross-linkers per molecule. This could be due to error in the SEC analysis, as a result of using materials dissimilar from the UPEs to calibrate the molecular weight vs. retention time curve. Another possibility is that the low molecular weights are purposefully used to maintain low resin viscosity and are a reason for the relatively poor mechanical properties of these UPE resins. In this case, many of the UPE monomers act as plasticizers (no FA or MA functionality) or reactive diluents (one FA or MA per molecule), while only some act to crosslink the polymer (two or more FA or MA per molecule). On the other hand, BBR and BFR had only slightly less than two vinyl groups per UPE, indicating these are relatively good cross-linkers and, as will be shown, have improved mechanical properties as a result. Based on the similarities of the SEC and NMR results, the assumption that HEX is used to formulate the Bondo repair putties is correct.

4.5 Optical Microscopy Analysis

The inorganic components were also analyzed to determine content and composition. Figure 10 shows 10× micrographs of glass fibers from Bondo BG. Figure 10a shows these fibers as originally separated, while the fibers in figure 10b were rinsed with acetone to remove non-fibrous matter. The milled glass fibers are a fairly close match while the chopped glass fibers are far too wide (figure 11).

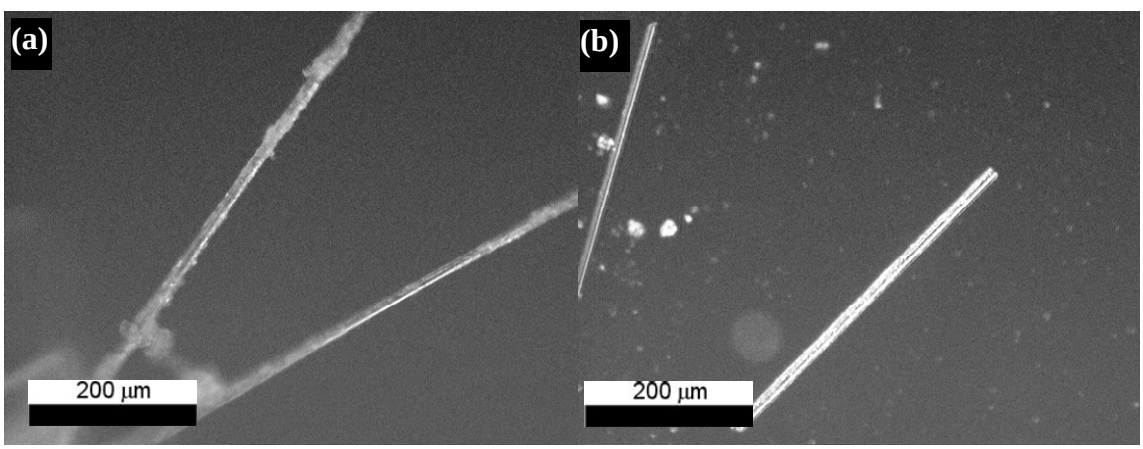

Figure 10. The 10× micrographs of Bondo BG fibers (a) as prepared and (b) cleaned with acetone wash.

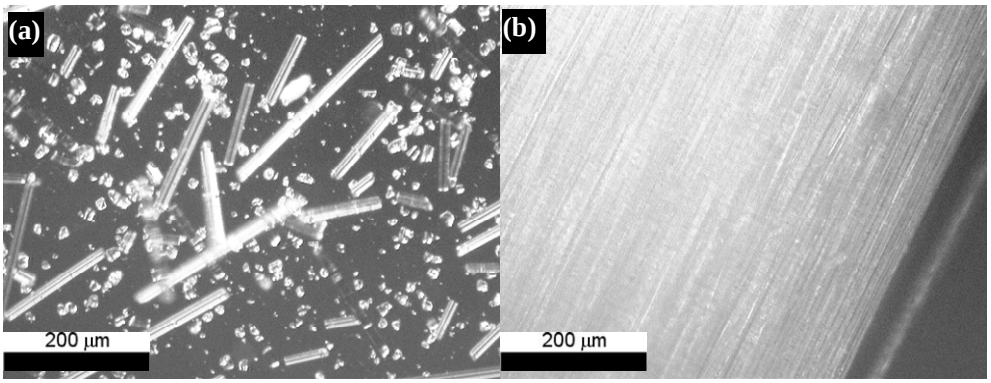

Figure 11. The 10× micrographs of (a) milled glass fibers and (b) chopped glass fibers.

BBF, BAP, and all of the Evercoat putties had a layer of foam after component separation, as shown in figure 2. The glass microspheres (figure 12a) are nearly identical and of similar size to the foam layer (figures 12b and c). Therefore, it is likely that the foam layer consists of microspheres. Microspheres are hollow and therefore have a very low density, explaining why they moved to the top during centrifugation. The sizes were measured using Paint Shop Pro v9.01 (JASC Software, 2004) to determine the width of four bubbles in each micrograph in pixels and multiplying by 1.297 µm/pixel; the average sizes are listed in table 7. The size of K37 is accurate because the 3M Scotchlite product information sheets show that 80% of the glass microspheres have dimensions ranging from 20 to 80 µm (*36*).

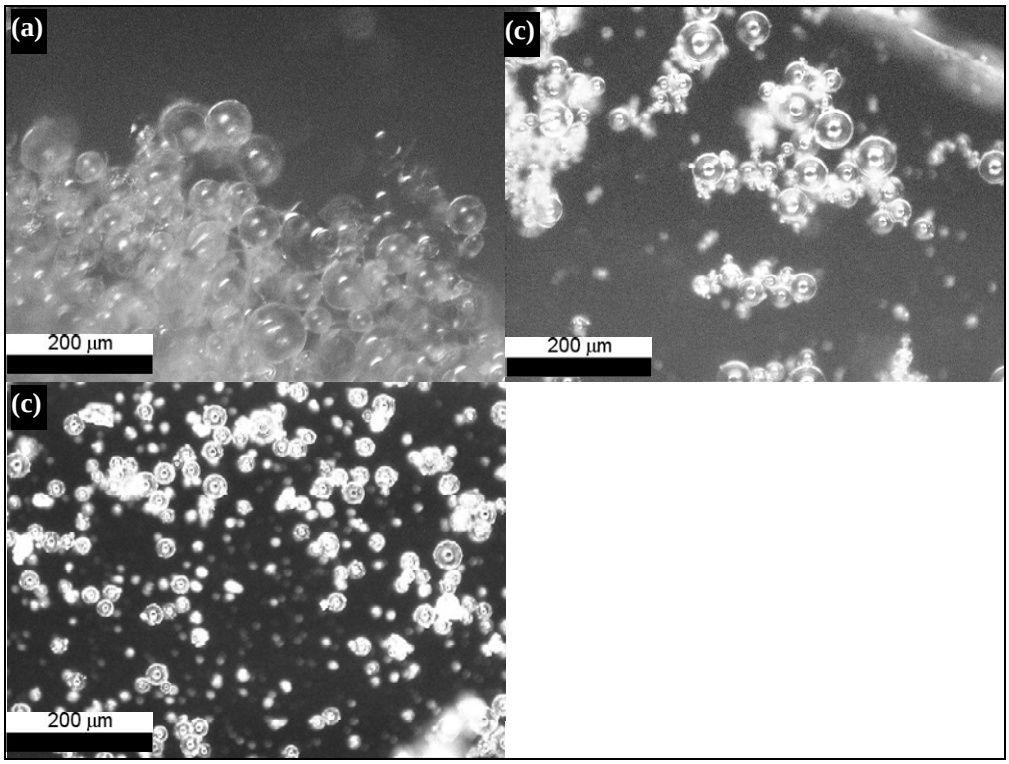

Figure 12. The 10× micrographs of (a) K37 Scotchlite glass microspheres, (b) BBF "foam" layer, and (c) EMG "foam" layer.

Table 7. Microsphere size.

Source of Glass Microspheres	Experimental Microsphere Diameter (µm)
K37 Scotchlite	64
BBF	32
EMG	24

The inorganic phases of BBF and BAP appeared similar, as shown in figure 13, as do the inorganic phases of EBF, ERAGE, and EMG. Aside from the fiber glass portion, the inorganic portion appears similar to that of BBF and BAP. Figure 14 shows micrographs of talc, magnesium carbonate, and sodium metaborate. These micrographs appear to match portions of the inorganic layers shown in figure 14, although given the variety of minerals, mineral processing conditions, and mineral sources for a specific mineral, the similarity is not sufficient to identify these components in the inorganic samples. Of the Evercoat inorganics, EG appears to be the coarsest, followed by EBF, ERAGE, and EMG. The glass strands in BG and EG appear to be similar in width. Too few whole strands are visible to characterize their length, although it is reasonable to assume that they are on the order of 1 mm long.

4.6 X-ray Fluorescence (XRF) Analysis of Inorganic Particulate Fillers

The number of fillers that can be used in a repair putty or filler is nearly limitless (*22*), so when armed with only the overall elemental composition of a mixture of fillers, it is impossible to determine which elements come from which minerals without making several clarifying assumptions. First, talc ($Mg_3Si_4O_{12}H_2$) should be by far the largest source of Si, so it was assumed that all of the Si was due to talc. This allowed the amount of Mg in talc to be calculated, and any remaining Mg was assumed to come from $MgCO_3$. The only Ca source was assumed to be $CaCO_3$. $MgCO_3$ and $CaCO_3$ may exist not as separate entities, but instead as a single mineral, dolomite ($MgCa(CO_3)_2$). This analysis does not differentiate between dolomite and equimolar amounts $MgCO_3$ and $CaCO_3$. All sodium was assumed to come from sodium metaborate dihydrate ($NaBO_2{\cdot}2H_2O$). Fe was present in most samples; there are several minerals that contain Fe, and no suitable method was available to discern which one(s) is (are) the Fe source, so Fe is reported only as elemental Fe. EMG required a slightly modified approach for several reasons: Mg limited the possible amount of talc, not Si (so the leftover Si was assumed to be SiO_2); Ti was present (assumed to be from TiO_2, a common white pigment (*22*), and also listed in the MSDS [*20*]); and Zn was present (assumed to be elemental zinc, a common corrosion inhibitor [*22*]). All other elements were either not detected or were present only in trace quantities.

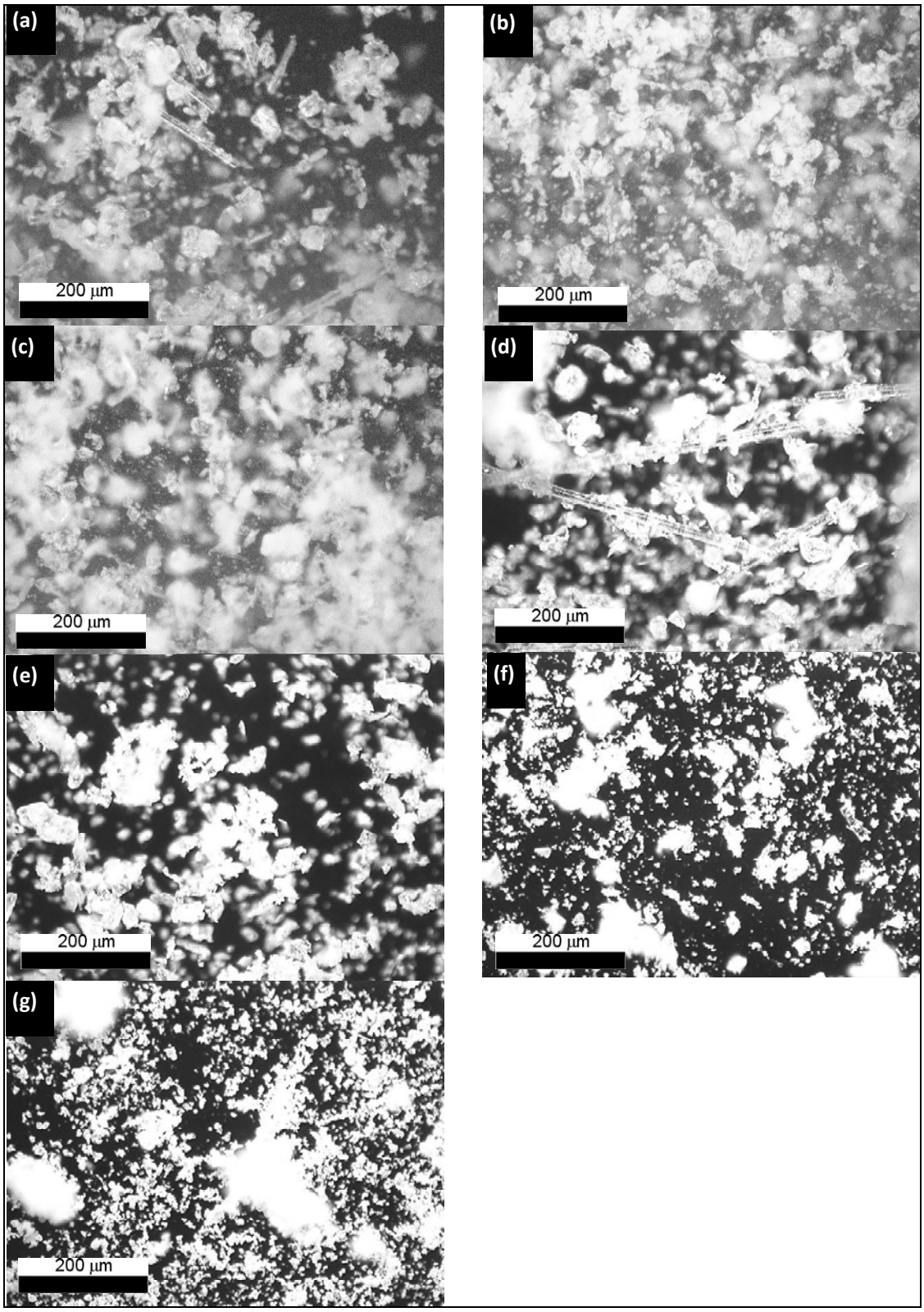

Figure 13. The 10× micrographs of inorganic layer found in (a) BG, (b) BBF, (c) BAP, (d) EG, (e) EBF, (f) ERAGE, and (g) EMG. Each micrograph covers ~0.83 × 0.62 mm.

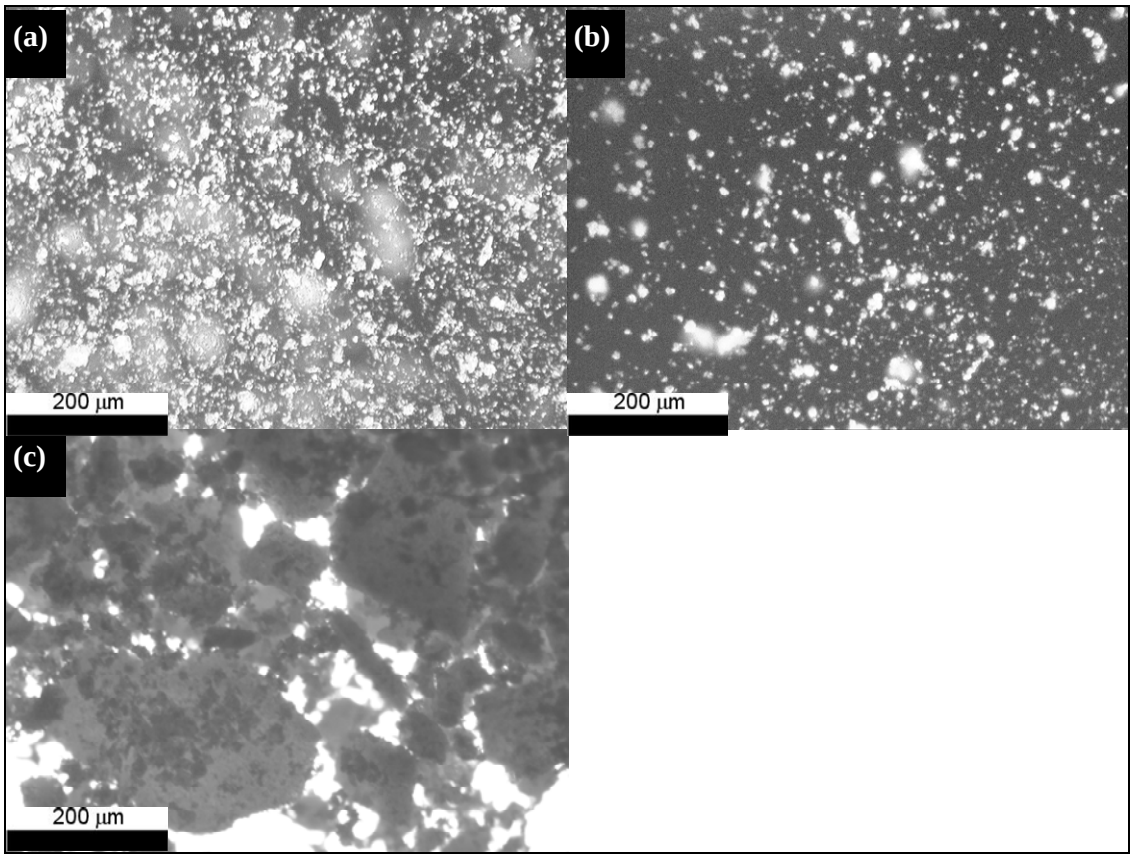

Figure 14. Micrographs of (a) talc (10×), (b) magnesium carbonate (20×), and (c) sodium metaborate (5×).

The compositions resulting from the XRF analysis can be found in table 8. Notice that most fillers have calculated talc compositions of above 70%—this is likely high due to the assumption that talc is the only source of Si (fumed silica, or SiO_2, is a common thickener used in repair products, and BG and EG also have fibrous glass filler, which is ~ 70% SiO_2 [*22*]). The fillers in BBF and BAP are identical, within the accuracy of the XRF experiment and analysis, and EBF and ERAGE are very close. Both of the glass-reinforced products (BG and EG) have very little if any $NaBO_2$. $NaBO_2$ drastically increases the viscosity of these repair products, as does the glass filler—having both would probably result in a product that is too viscous to apply. EMG, which is designed to be applied on top of a repair prior to priming and painting, contains a large amount of Ti, possibly as a pigment to mask the color of the resin so that it does not bleed through the paint coating. EMG also contains a large amount of Zn, which may be used as a corrosion inhibitor.

Table 8. Mass compositions of the filled repair products assuming that only the minerals shown are present in the filler mixture.

Component	Talc	$MgCO_3$	$NaBO_2$	$CaCO_3$	Fe	SiO_2	TiO_2	Zn
BG	72	13	0.4	13	2.1	—	—	—
BBF	76	17	3.4	0.5	2.7	—	—	—
BAP	75	18	3.4	0.6	2.7	—	—	—
EG	83	13	0.4	2.2	1.8	—	—	—
EBF	73	15	2.6	8.4	1.6	—	—	—
ERAGE	68	16	0.5	14	1.4	—	—	
EMG	65	—	—	22.7	0.4	1.9	4.5	5.1

4.7 Thermogravimetric Analysis

TGA results showing the mass loss of component A putties as a function of temperature are shown in figure 15. The char contents at 55 ^{o}C and 800 ^{o}C are shown in table 9, along with the difference between the char contents and the amount of inorganics (including foam) from the component separation. At 550 °C, all of the organic components should have burned, leaving only inorganic fillers behind. The fillers should be largely unaffected by temperatures up to 800 ^{o}C, but some may partially burn between 550 °C and 800 °C. Thus, a rough estimate of the inorganic content (including the "foam" from section 4.1) can be obtained from the char content at 550 °C.

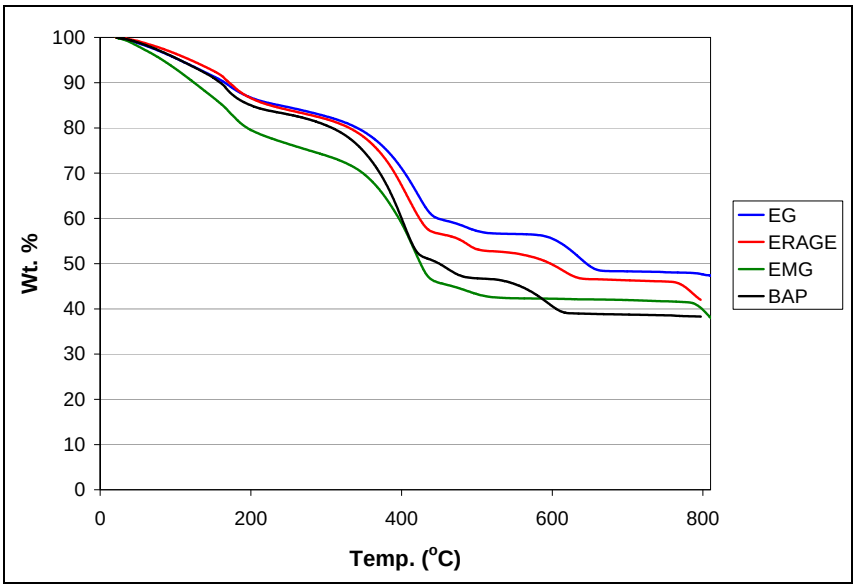

Figure 15. Weight loss as a function of temperature for Bondo and Evercoat repair putties (component A).

Table 9. Char contents of uncured component A from several repair putties at 550 °C and 800 °C.

Product	Char (%)		Percent Difference From Component Separation		Loss (%)
(Comp A)	550 °C	800 °C	550 °C	800 °C	550–800 °C
BG	47.8	40.9	–9.0	–15.9	7.0
BBF	47.3	40.8	–5.4	–11.9	6.5
BAP	45.5	38.3	–1.0	–8.2	7.2
EG	56.6	47.7	–0.2	–9.1	8.9
EBF	49.7	41.5	0.0	–8.2	8.2
ERAGE	52.3	42.1	0.4	–9.8	10.2
EMG	42.3	39.9	–1.2	–3.6	2.4

EMG, which has a lower filler content and higher styrene content, loses more mass than the other repair products and also has a much higher initial mass loss as shown by the strong negative slope in figure 15.

The char contents at 800 °C are 4% to 16% lower than the sum of the inorganic and "foam" components (from table 3). This is likely due to some of the inorganic components burning, such as insoluble surface treatments on the inorganic components, resulting in a lower apparent inorganic content. The char at 550 °C gives a much better indication of the actual amount of inorganics with little deviation from the component separation results, except for BG and BBF which had inorganic contents of 9.0% and 5.4%, respectively, lower than the component separations.

Figure 16 shows the derivative weight loss as a function of temperature. At temperatures below 200 °C, EMG clearly loses mass more quickly than any other product, probably because it has the highest styrene content and is the least viscous, thus allowing evaporation to proceed more readily. BAP loses a little more mass during the 170 °C and 407 °C transitions and a bit less in the 470 °C transition. All three had similar weight loss during the 598 °C transition. In general, the Evercoat and Bondo products matched up well, indicating, once again, that the UPEs are similar and the organic binder ratio to the inorganic filler is similar over both product lines (although not between product lines). The weight loss and derivative weight curves for BG, EBF, and BBF are not shown because they are very similar to the other curves.

Figure 17 shows the TGA weight loss as a function of temperature results for the cured Bondo repair resins, and figure 18 shows the corresponding derivative weight loss. The cream hardener, component B, was mixed with component A to form the polymer. Component B was used in the amount of 1.8 wt%.

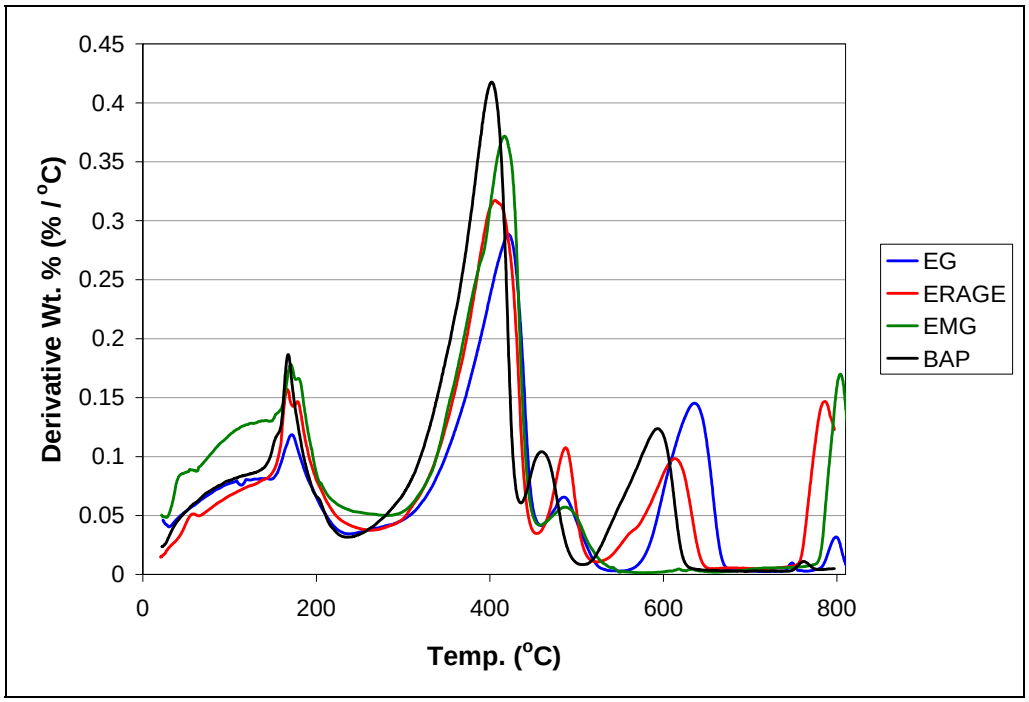

Figure 16. Derivative weight loss as a function of temperature for Bondo and Evercoat repair putties (component A).

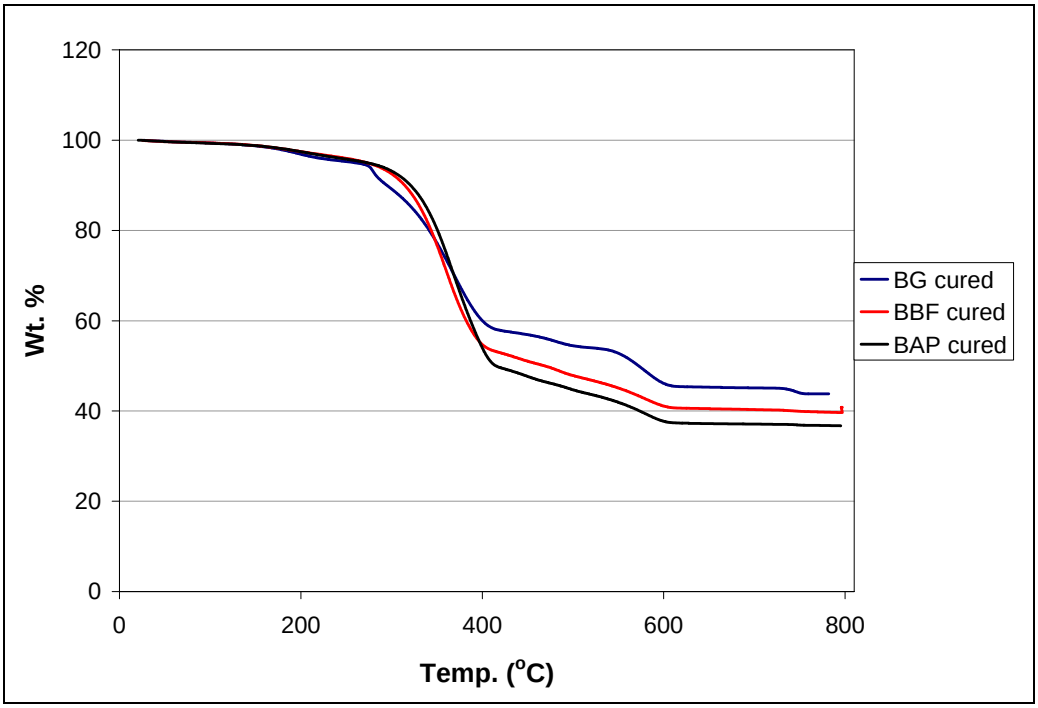

Figure 17. Weight loss as a function of temperature for cured Bondo polymers.

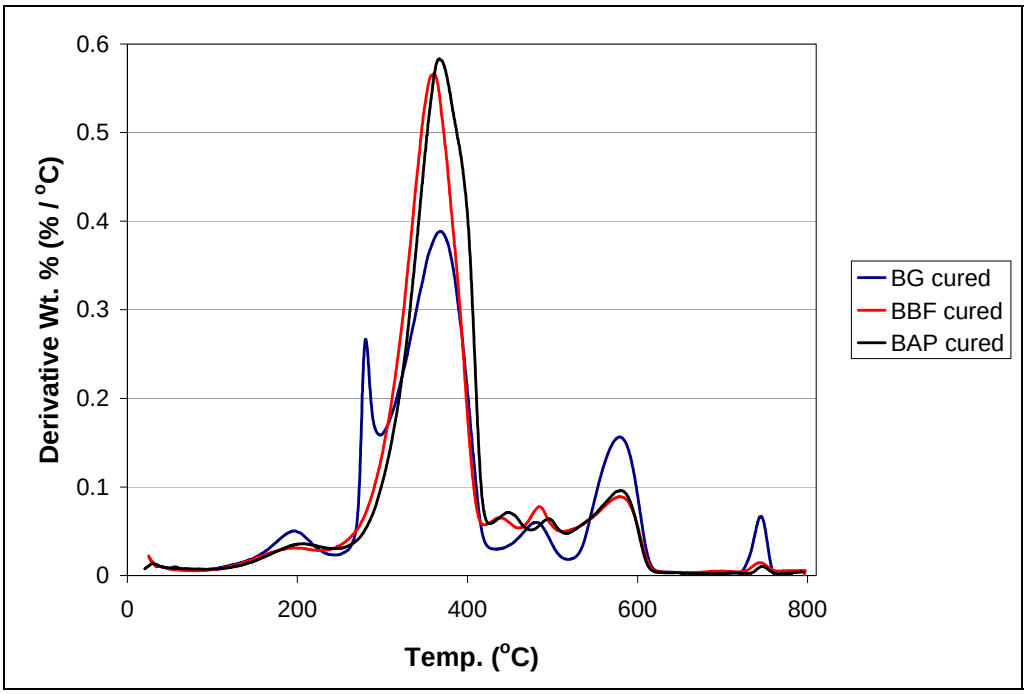

Figure 18. Derivative weight loss as a function of temperature for cured Bondo polymers.

All samples lose ~5 wt% of their mass below 200 °C, which could possibly be a result of unreacted styrene and components in the initiator solution evaporating from the sample. Char remainders of entire polymers are shown in table 10. The mass loss is scattered around the mass loss for the uncured component A TGA results. As seen for the uncured samples, BAP lost the most mass overall. Figure 18 shows the derivative mass as a function of temperature. BG lost mass earlier than the others at 200–283 °C, possibly due to the glass component. BG had the smallest mass loss at the 375 °C decomposition and the largest mass loss at 586 °C and 749 °C. BAP has two decompositions at 455 °C and 504 °C, whereas BBF and BAP only have one decomposition temperature at ~490 °C. The specific pyrolysis causing the individual derivative weight loss peaks has not been identified, but given the similarity in the NMR spectra of the organic portion of the Bondo putties and the high temperature of these decompositions, it is unlikely that the differences in the TGA runs are due to differences in resin composition but instead are a result of different filler content.

Table 10. Char contents of cured Bondo repair resins at 550 °C and 800 °C.

Product	**Char (%)**		**Percent Difference From Uncured TGA**		**Loss (%)**
(Comp A + B)	**550 °C**	**800 °C**	**550 °C**	**800 °C**	**550–800 °C**
BG	52.8	43.8	+5.0	+2.9	9.0
BBF	45.1	40.8	–2.2	0	4.3
BAP	41.9	36.7	–3.6	–1.7	5.2

4.8 Component Concentration in Commercial Repair Resins

Based on the component separation, NMR, TGA, XRF, and microscopy results, the approximate composition of the commercial repair putties can be determined (table 11). The UPE content was determined from the component separation, the styrene content from NMR, and the four main components were normalized to 100%. The inorganic portion was calculated from the XRF data, with 3 wt% fibrous glass added to BG and EG. The "UPE Resin" columns normalize the styrene and UPE contents to 100 wt%. From table 11, it is evident that the compositions of these resins are fairly consistent (at least within a given manufacturer's product line).

Table 11. Overall constituents of repair putties and resins, based on the experimental data given in this work.

Type	Repair Putty				Inorganic Portion (Based on Total Putty Mass)						UPE Resin	
	UPE (wt%)	Styrene (wt%)	Inorganic (wt%)	MS (wt%)	Talc	$MgCO_3$	$NaBO_2$	$CaCO_3$	Fe	FG	UPE	Sty
HEX	76	24	0	0	0	0	0	0	0	0	76	24
BG	33	10	57	0	39	7	0	7	1	3	76	24
BBF	37	10	47	5.6	36	8	1.6	0.3	1.2	—	78	22
BAP	40	12	43	4.6	33	8	1.5	0.3	1.2	—	77	23
BBR	72	28	—	—	—	—	—	—	—	—	72	28
BFR	72	28	—	—	—	—	—	—	—	—	72	28
EG	30	12	57	0.8	45	7	0	1	1	3	72	28
EBF	35	12	47	5.3	34	7	1.2	4	0.7	—	74	26
ERAGE	35	13	48	3.5	33	8	0.2	7	0.7	—	74	26
—	—	—	—	—	**Talc**	**SiO_2**	**TiO_2**	**$CaCO_3$**	**Fe**	**Zn**	—	—
EMG	36	22	35	7.4	23	0.7	1.6	8	0.2	1.8	64	36

The Evercoat putties contain a higher styrene-to-UPE ratio relative to the Bondo putties. The results indicate that BG, BBF, BAP, and HEX likely use the same organic resin and similarly for EG, EBF, and ERAGE. Thus, any differences in the properties (e.g., modulus and viscosity) of these products are likely caused by subtle differences in the composition. EMG is the same UPE resin as the other Evercoat resins but contains added styrene. BBR and BFR resins are distinctly different UPE monomers with higher unsaturation content and different molecular structures to have higher T_g and rigidity. Specialty putties (EMG) and neat resins (BBR and BFR) contain more styrene—from 22 to 28 wt%.

The fiber-reinforced glass repair putties EG and BG contained similar inorganic additives (mostly talc, with some $MgCO_3$ fibrous glass, and $CaCO_3$). The non-glass-reinforced putties BBF, BAP, EBF, and ERAGE also were very similar containing 33–36 wt% talc, 7–8 wt% $MgCO_3$, and 3.5–5.6 wt% glass microspheres. Evercoat products tended to have relatively high contents of $CaCO_3$ (4–7 wt%), whereas Bondo products had only ~0.3 wt% of it. Bondo putties also tended to use slightly higher amounts of $NaBO_2$ relative to the Evercoat putties.

Although the analysis confirmed the use of many of the components listed on the MSDS for Bondo products (*6*, *7*, *13–15*), there are some differences. In particular, the measured talc content is much higher, and the $NaBO_2$ and $MgCO_3$ contents are lower than listed for Bondo products. On the other hand, the measured component concentrations are similar to what was listed on the MSDS for Evercoat products (*17–20*).

4.9 Rheology and Viscosity Results

UPE repair putties are quite viscous but display shear-thinning behavior (figure 19). Below 0.004 1/s, BG, BBF, and BAP are Newtonian but shear thin at higher shear rates. Component B is only Newtonian at 0.00125 1/s and lower, but otherwise shear-thins. The Ostwald-de Waele power-law model was used to fit the experimental data (*37*, *38*):

$$\eta = K\dot{\gamma}^{n-1}, \tag{6}$$

where K reflects the magnitude of the viscosity, with higher values indicating more viscous fluids, and n affects the shear-thinning slope. The parameter values are listed in table 12, and the fits to the data were good in the shear-thinning range, as shown in figure 19.

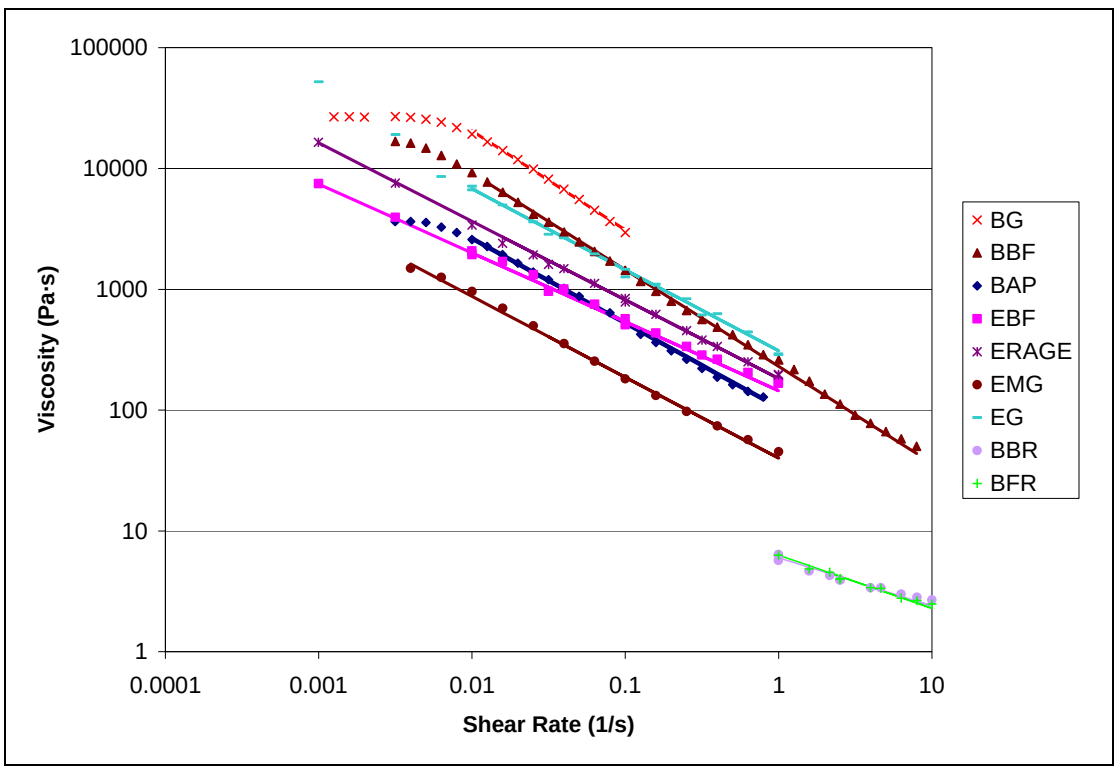

Figure 19. Viscosity as a function of shear rate for Bondo and Evercoat products.

Table 12. The Ostwald-de Waele power-law model parameters for repair putties.

Power Law Parameter	BG	BBF	BAP	BBR	BFR	EG	EBF	ERAGE	EMG
κ (Pa.s)	470	230	105	6.0	6.3	310	145	183	40
n	0.18	0.2	0.3	0.60	0.56	0.33	0.43	0.35	0.33

BG is the most viscous putty overall, and EG is the most viscous in the Evercoat product line, likely due to the glass fibers. EMG is designed to be used as a sealant over existing unpainted repairs and is the least viscous, which is a result of its higher styrene content and lower inorganics content. In general, Evercoat products are slightly less viscous than Bondo repair putties, due to their higher styrene content. The exponent "n" parameter ranges from 0.33 to 0.43 for the Evercoat products, and the Bondo products have an "n" parameter from 0.18 to 0.3, which indicates a higher degree of shear thinning for the Bondo products, likely due to the lower styrene content. Excluding EMG, the viscosity of all of the repair products are within 1 order of magnitude at any given shear rate.

HEX resin did not display any shear thinning characteristics and had a steady state shear viscosity of 0.59 Pa·s over the shear rate range of 1 to 200 s^{-1}. Thus, it is apparent that the shear thinning and high viscosities of the filled putties is largely due to the fillers. On the other hand, BBR and BFR did shear thin (figure 19) despite not having any filler content. The shear thinning character may be the result of increased hydrogen bonding in BBR and BFR as a result of the differences in the chemical makeup. Shear thinning may be the result of the breakdown of such chemical interactions with increasing shear rate.

4.10 Dynamic Mechanical Analysis Results

The dynamic mechanical properties for typical Bondo resins are shown in figure 20 and table 13. BBF and BAP are nearly identical, and EBF and ERAGE are very similar as well. The storage modulus decreased slowly with temperature at low temperatures in the glassy regime (~50 °C to 0 °C). At temperatures above 0 °C through 50 °C, the storage modulus decreased rapidly with temperature. At higher temperatures in the rubbery regime, the modulus was fairly constant with temperature. The modulus was clearly higher for the BG and EG samples than it was for any of the other samples (figure 20 and table 13) at all temperatures. This is likely due to the use of high-aspect-ratio glass fiber reinforcement.

The T_g according to the loss modulus maximum was similar for all three Bondo putties, ranging from 22.2 °C to 25.5 °C. BG had a slightly higher T_g and a lower tan delta maximum temperature than BBF or BAP, which could be due to slight differences in the reinforcement used. EMG had a substantially higher T_g and tan delta maximum temperature than any of the other Evercoat products—this is most likely due to the higher styrene content (~37.7% of the resin [ignoring fillers] vs. ~27% of EG, EBF, and ERAGE). The broader loss modulus peak for

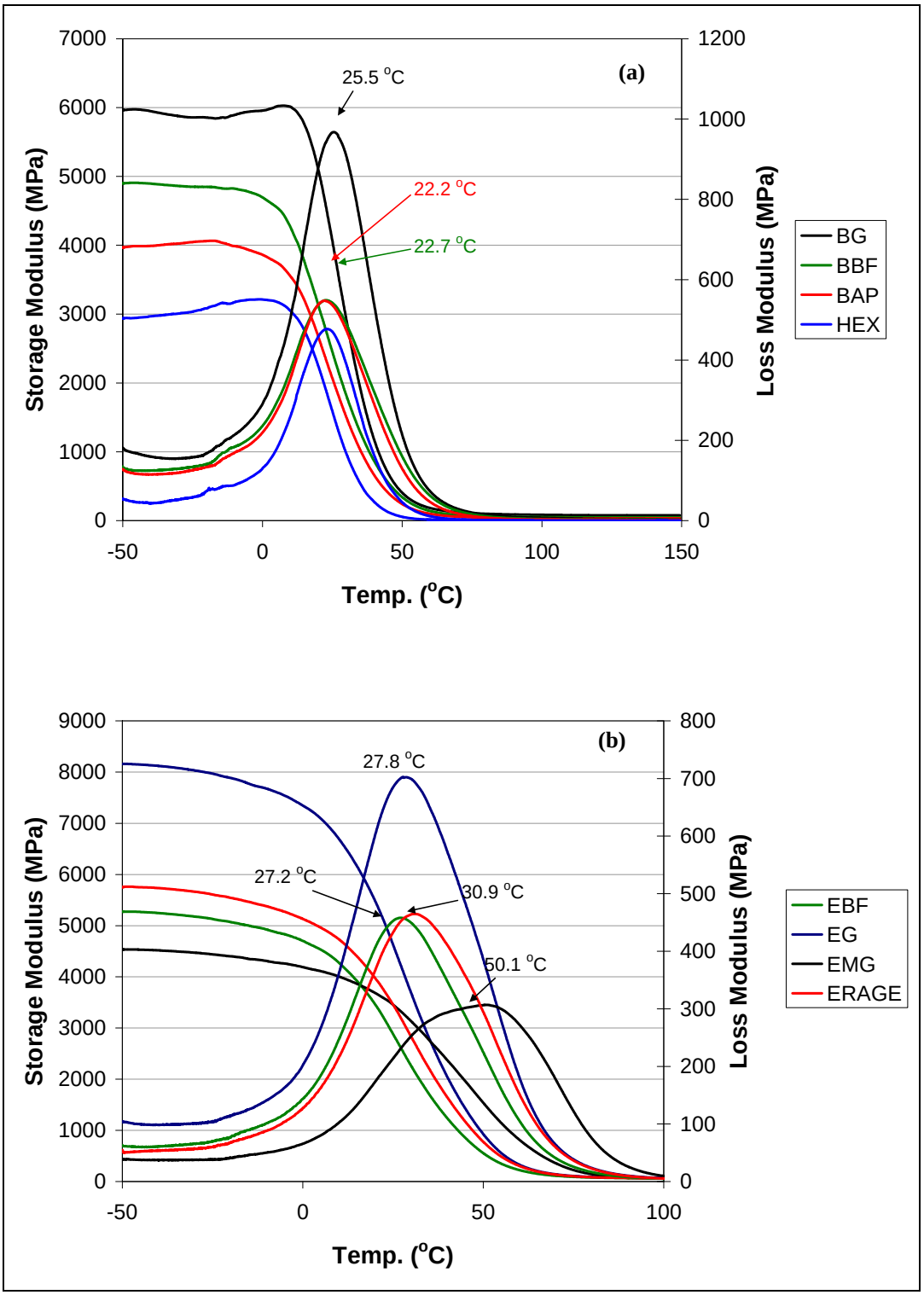

Figure 20. Dynamic mechanical properties as a function of temperature for (a) Bondo and (b) Evercoat repair putties.

Table 13. Dynamic mechanical properties for Bondo resins.

Product	E'(–50 °C) (GPa)	E'(25 °C) (GPa)	T_g (E" max) (°C)	Tan Delta Max (°C)
BG	6.0	4.0	26	49
BBF	4.9	2.5	23	50
BAP	4.0	2.1	22	50
BBR	4.0	2.7	37	83
BFR	4.2	3.0	43	85
EG	8.2	4.6	28	61
EBF	5.3	2.9	27	59
ERAGE	5.8	3.4	31	62
EMG	4.5	3.5	50	76
HEX	2.9	1.6	23	51

EMG is likely a function of the higher vinyl content and different filler content relative to the other Evercoat products. The Evercoat products had higher T_g's than the Bondo products, likely due to their slightly higher styrene contents. On the other hand, the neat resin HEX had approximately the same T_g as BBF and BAP, verifying that the organic resin in BBF and BAP is the HEX resin. BG had a slightly higher T_g than HEX because of the high reinforcement of the BG fillers.

BBR and BFR liquid repair resins had higher T_g than the other resins and putties and also had higher moduli than the HEX resin. This is expected because of the higher styrene content, higher unsaturation content, and different chemical composition. In particular, the replacement of some of the DEG with Egly and the replacement of PA with TP are expected to increase stiffness. Despite the slightly higher T_g according to the loss modulus peak for BFR relative to BBR, the difference is believed to be insignificant. The moduli as a function of temperature were very similar for both resins, and the tan delta values are nearly identical (figure 21).

4.11 Flexural Results

The flexural results of Bondo resins are shown in table 14. Essentially, BG had the highest modulus (~2 GPa) and highest strength (~22 MPa) as a result of the relatively long glass fibers added to the resin. BAP had slightly higher flexibility and modulus than BBF. Therefore, although BBF and BAP appear quite similar, slight differences in the filler content likely contribute to these differences. The low modulus and strength of these materials are likely due to the low cross-linker content and low rigidity of these resins. The flexural results of BBR and BFR are considerably higher than that of the repair putties (BG, BBF, and BAP) and unfilled resin (HEX) because of their higher cross-link density and difference in resin molecular structure. The results of the unfilled HEX show that the fillers used increased the strength and modulus immensely, although the strain to failure decreased. This is expected as fillers generally make the sample more rigid but less flexible (*22*). Note that the flexural moduli from flexural

testing were lower than as determined by DMA. The reason for this is the samples are not equilibrated at room temperature in the DMA testing as a result of the temperature ramp used, and both tests operate at different rates, which is known to affect the properties of viscoelastic materials.

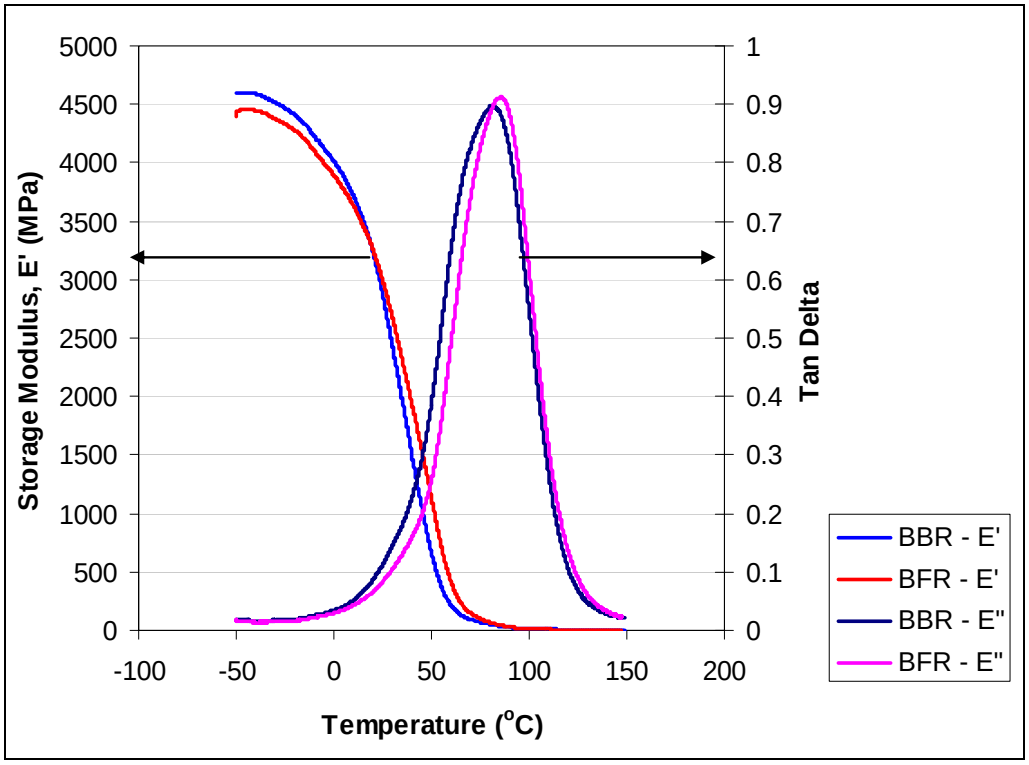

Figure 21. DMA of the BBR and BFR resins.

Table 14. Flexural results for Bondo resins.

Bondo Type	Flexural Modulus (GPa)	Flexural Strength (MPa)	Maximum Strain (%)
HEX	0.224 ± 0.015	7.7 ± 0.4	12.73 ± 1.18
BG	1.97 ± 0.25	22.4 ± 2.2	6.95 ± 1.71
BBF	0.73 ± 0.04	12.7 ± 0.7	5.08 ± 0.79
BAP	0.89 ± 0.04	12.8 ± 1.0	8.76 ± 1.46
BBR/BFR	3.16 ± 0.09	32.2 ± 5.2	1.15 ± 0.35

5. Conclusions

This study provides basic rheological, thermal, and mechanical properties of commercially available repair putties, as well as the composition of these products. The most commonly used commercially available repair putties contain 10–15 wt% styrene, 30–40 wt% UPE monomers, and 48–58 wt% inorganic content.

Evercoat putties used more styrene than Bondo putties. Other putties and other repair resins contain up to 30 wt% styrene. Most repair putties used similar UPE monomers, which are low molecular weight polymers of DEG and PA/FA/MA/other acids. Liquid repair resins BBR and BFR are significantly different than the repair putty polyesters. BBR and BFR are low molecular weight polymers of DEG/Egly/other alcohols and TP/PA/FA/MA/other acids and contain 50% more unsaturation sites per mol of UPE. SEC results were used to estimate the molecular weights of the UPE monomers at ~950–1350 g/mol. Hexion 713-6150 was used to formulate Bondo repair putties as shown from the similarity in the composition of this base resin to the organic resin portion of the repair putties, as well as similarities in T_g.

The repair putties all exhibit different degrees of shear-thinning behavior. Also, their viscosities differ widely, with some (EG) more than 10× higher than others (EMG) at a given shear rate. They have T_g's ranging from 23 °C to 31 °C, room temperature storage moduli spanning from 2.1 to 4.6 GPa, flexural moduli ranging from ~0.7 to ~2 GPa, and flexural strengths ranging from ~12 to 24 MPa. The resins with FG have higher viscosities, moduli, and strength than other putties.

These properties provide important benchmark characteristics that must be more or less met by environmentally friendly, HAP-free repair resins developed at ARL/Drexel University utilizing renewable fatty acid-based monomers.

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List of Symbols, Abbreviations, and Acronyms

ARL	U.S. Army Research Laboratory
BAP	Bondo All-Purpose Putty
BBF	Bondo Body Filler
BBR	Bondo Boatyard Resin
BCH	Blue Cream Hardener, used to cure Evercoat products
BFR	Bondo Fiberglass Resin
BG	Bondo Glass
DEG	diethylene glycol
DMA	dynamic mechanical analysis (polymer thermomechanical analysis)
E’	storage modulus
E”	loss modulus
EBF	Evercoat Lite Weight High Production Filler
EG	Evercoat Glass Lite Filler
Egly	ethylene glycol
EMG	Evercoat Metal Glaze
ERAGE	Evercoat RAGE – Premium Liteweight Filler
FA	fumaric acid
FG	fibrous glass
HAP	hazardous air pollutant
HEX	Hexion 713-6150, neat resin used in BG, BAP, and BBF
M	magnesium carbonate, $MgCO_3$
MA	maleic acid
MSDS	material safety data sheet
N	sodium metaborate, $NaBO_2$

NMR	nuclear magnetic resonance
PA	phthalic acid
RCH	Red Cream Hardener, used to cure Bondo products
SA	suberic acid
SEC	size exclusion chromatography
TP	terephthalic acid
tan(δ)	ratio of loss modulus to storage modulus
T_g	glass transition temperature of polymer
TGA	thermogravimetric analysis
THF	tetrahydrofuran
UPE	unsaturated polyester
VE	vinyl ester
wt%	weight percent
XRF	x-ray fluorescence

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