

Risks involved in curing vinylester resins using microwaves irradiation

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Abstract: Preliminary studies have been carried out to cure vinylester particle reinforced resins in microwaves to reduce shrinkage of the composites. The results were encouraging. With an exposure time of 35 to 40 seconds and a power level of 180 W, the shrinkage of 50 ml and 200 ml composite samples, flyash particulate reinforced vinylester resin, approached zero percent. Despite the success, there are risks in the process of curing the vinylester resins by microwave irradiation. The styrene vapour emitted from the resins is harmful to human beings and becomes an inhalation hazard. In addition, the styrene vapour in the cavity of the microwave oven may be ignited arcing within the oven. Alternatively, arcing from the high voltage (HV) transformer behind the oven cavity may ignite vapour leaking from the cavity. Even if this does not happen, the concentration of the styrene vapour in the oven cavity is high may lead to explosions. Another risk is posed by the hardening agent, methyl ethyl ketone peroxide (MEKP), which undergoes an exothermic reaction when irradiated with microwaves and could spontaneously ignite. However, if the usual rate of 1-2% of it is used in hardening the resin, most of its dangerous properties will disappear (Sweet, undated). MEKP is itself poisonous and has to be handled with care.

Keywords: Vinylesters, shrinkage, microwaves, relative complex permittivity, loss tangent, styrene and methyl ethyl ketone peroxide (MEKP).

Introduction

The most common thermosets used as composite matrices are unsaturated polyesters (UP), epoxies and vinylesters. Unsaturated polyesters dominate the market, whereas epoxies are preferred in high-performance applications. Unsaturated polyester offers an attractive combination of low price, reasonably good properties, and simple processing. However, basic unsaturated polyester formulations have drawbacks in terms of poor temperature and ultra-violet tolerance. Where mechanical properties and temperature tolerance of unsaturated polyesters no longer suffice, epoxies (EP) are often used due to their significant superiority in these respects. Of course, these improved properties come at a higher price and epoxies are used most commonly in areas where cost tolerance is highest [1]. In addition to inhalation hazard, the styrene vapour emitted from the vinyl ester resins may be ignited by arcing as previously mentioned. This paper outlines the risks involved in curing the resins by microwaves and suggests some ways to avoid the hazards.

Vinyl esters and their crosslinking

There are three families of vinylesters. The first and most common used family is based on the reaction between methacrylic acid and diglycidylether of bisphenol A (DGEBA) as shown in Figure 1 [1]. From the corrosion standpoint, they resist a wide range of aggressive chemicals well. In particular, they outperform other resins of the family in their resistance to high pH caustic solutions. The second vinylester family uses a novolac epoxy resin as its starting point. The resulting epoxy novolac vinylester resins have a higher crosslink density than the bisphenol A epoxy vinylester resins. This means that it is more difficult for chemicals to penetrate the matrix, and

they have improved resistance to organic solvents and mineral acids. The final category of vinylester resin is formed when tetrabromo bisphenol-A (TBBA) is used in the manufacture of the resin. Up to 20 percent of bromine is bound into its structure and is designed to have good fire retardancy [2]. Being an unsaturated polyester-epoxy compromise, vinylesters are more likely to be used in an application where an unsaturated polyester does not quite fulfil the requirements, rather than in an application where an epoxy represents an overkill. An application area in which vinylesters have been particularly successful is the corrosive industrial environment.

The polymerisation product between methacrylic acid and bisphenol A is vinylester, which can be a highly viscous liquid at room temperature or a low melting point solid, depending on the acid and bisphenol A used. For further processing, the polymer is dissolved in a low molecular monomer, or reactive diluent, usually styrene; the result is a low viscosity liquid referred to as resin. The styrene content of the vinylester resin used in this research is 50% parts by weight. With the addition of a small amount of initiator to the resin the crosslinking reaction, or curing, is initiated. The initiator used is an organic peroxide, eg methyl ethyl ketone peroxide (MEKP). The added amount is usually 1 to 2 percent by weight. The peroxide decomposes after it is added to the resin and the reaction is exothermic. The initiator is a molecule that produces free radicals. The free radical attacks one of the double bonds on the ends of the polymer and bonds to one of the carbon atoms, thus producing a new free radical at the other carbon atom, see the initiation step of Figure 2, which illustrates the whole crosslinking process. This newly created free radical is then free to react with another double bond. Since the small monomer molecules, the styrene molecules, move much more freely within the resin than the high molecular weight polymer molecules, this

double bond very likely belongs to a styrene molecule, as illustrated in the bridging step of Figure 2. The bridging step creates a new free radical on the styrene, which is then free to react with another double bond and so on. Obviously the styrene is not only used as solvent, but actively takes part in the chemical reaction. In the crosslinking of thermosets, monomers are consequently called building blocks and initiators are called catalysts or curing agents.

Figure 3 shows typical temperature time relations for crosslinking of a vinyl ester following addition of initiator. The three solid curves on the right hand side of the figure represent room temperature crosslinking of vinyl esters. The different curves illustrate different amount of initiator, inhibitor, accelerator, ambient temperature and humidity or volume of resin. A reduced amount of initiator and accelerator, as well as an increased amount of inhibitor, leads to later crosslinking at lower exotherm temperature, and vice versa. The larger the volume of the resin, the faster the reaction will be. Crosslinking reactions are exothermic in nature, and reactions occur faster at higher temperatures. When there is a large volume of resin, exothermic heat produced cannot easily escape, therefore temperature builds up fast, which in turn accelerates the reaction rate, the process is known as “thermal runaway”. The temperature does not immediately increase after addition of an initiator despite free radicals being produced. The crosslinking reaction does not start and the temperature does not increase until all inhibitor molecules have reacted with free radicals, which corresponds to inhibition time. As crosslinking commences, the pot life is over. The resin becomes a rubbery solid quickly and the gel time is reached. The crosslinking activity now accelerates very rapidly until the increasing molecular weight of the crosslinking polymer starts restricting molecular movement, which occurs around the

maximum temperature, and the crosslinking gradually tapers off. On the other hand, the dashed line curve on the left-hand side of Figure 3 illustrates the hypothetical crosslinking as a result of the application of microwave to the resin. In this case, the inhibition time is short and maximum temperature is reached quickly. The maximum temperature reached is also expected to be higher. It is anticipated that the result of such a curing will reduce the shrinkage of vinyl ester [3].

Microwaves

Microwaves form part of a continuous electromagnetic spectrum that extends from low-frequency alternating currents to cosmic rays. These microwaves propagate through empty space at the velocity of light and their frequencies range from 300 MHz to 300 GHz. Industrial microwaves are generated by a variety of devices such as magnetrons, power grid tubes, klystrons, klystrodes, crossed-field amplifiers, travelling wave tubes, and gyrotrons [4]. Frequency bands reserved for industrial applications are 915 MHz, 2.45 GHz, 5.8 GHz and 24.124 GHz. At the customary domestic microwave frequency of 2.45 GHz, the magnetrons are the workhorse. Material processing falls into this category [4, 5]. Magnetrons are the tubes used in conventional microwave ovens found almost in every kitchen with power of the order of a kilowatt. Industrial ovens with output upto a megawatt are not uncommon.

The material properties of greatest importance in microwave processing of a dielectric are the complex relative permittivity $\epsilon = \epsilon' - j\epsilon''$ and the loss tangent, $\tan \delta = \epsilon'' / \epsilon'$ [6]. The real part of the permittivity, ϵ' , sometimes called the dielectric constant, mostly determines how much of the incident energy is reflected at the air-sample interface,

and how much enters the sample. The most important property in microwave processing is the loss tangent, $\tan \delta$ or dielectric loss, which predicts the ability of the material to convert the incoming energy into heat. For optimum microwave energy coupling, a moderate value of ϵ' , to enable adequate penetration, should be combined with high values of ϵ'' and $\tan \delta$, to convert microwave energy into thermal energy. During microwave processing, microwave energy penetrates through the material. Some of the energy is absorbed by the material and converted into heat, which in turn raises the temperature of the material such that the interior parts of the material are hotter than its surface, since the surface loses more heat to the surroundings. This characteristic has the potential to heat large sections of the material uniformly. The reverse thermal effect in microwave heating does provide some advantages. These include:

- Rapid heating of materials without overheating the surface
- A reduction in surface degradation when drying wet materials because of lower surface temperature
- Removal of gases from porous materials without cracking
- Improvement in product quality and yield
- Synthesis of new materials and composites.

Risks of styrene

Health concerns with vinyl esters are considered synonymous with the most common crosslinking agent, the styrene, and not with the polymers themselves. Styrene is volatile and evaporates easily and becomes an inhalation hazard. The reported levels

that cause a specific acute reaction vary widely, partly because tolerance is individual and depends on build up, and partly because reactions are subjective. At concentrations in the range of 20-100 parts per million (ppm), styrene is a mild, temporary irritant to eyes and respiratory tract. Above 200 ppm styrene is a definite irritant causing central nervous system (CNS) depression, and above 500 ppm it is a severe irritant. The International Agency for Research on Cancer classifies styrene as a possible carcinogen. Measures to reduce styrene emission are therefore carried out. However, the United States Environmental Protection Agency (EPA) has not formally classified styrene as a carcinogen or listed it as such on the Integrated Risk Information System (IRIS) Database but its cancer classification of styrene for carcinogenic potential is under review [7].

The risk of acute styrene poisoning through inhalation is quite low since the human nose is extremely sensitive to the very characteristic styrene smell; the odour threshold is approximately 0.1 ppm. Styrene is said to have excellent warning properties, since the odour threshold is in orders of magnitude below permissible exposure level (PELs). Table 1 gives the time-weighted average (TWA) and short-term exposure level (STEL) in ppm for styrene in some English speaking countries [1]. It can be seen that the acceptable concentration of styrene varies greatly with the highest TWA and STEL in the United Kingdom. Long term occupational exposure to styrene increases the frequency of chromosome damage in one type of blood cells and may possibly cause brain damage at concentrations as low as 10 ppm. The obvious solution is to reduce styrene content in the resins so there is less that can evaporate. This, however, may reduce the fluidity of the resin. Another possibility is offered by low styrene emission (LSE) resins, which contain a substance that migrates to the

surface of the resin to create a thin film impenetrable to styrene. LSE resins do not reduce evaporation during spray-up, lay-up and rolling because it takes some time for the film to form. During crosslinking, evaporation may be reduced to half. Styrene is a mild to severe irritant to both skin and eyes upon contact. In terms of personal protection equipment (PPE) it is important to note that no glove material is good for long term exposure to styrene. Styrene is highly flammable, high vapour concentrations may cause explosions. Styrene vapour has a higher density than air and there is always a misconception that styrene flows along the floor. This is true in theory but the density difference between the styrene-containing air and the uncontaminated air is very little. Temperature difference and air movements are more critical and any settling tendency is obscured. The risk of the interaction of styrene vapour with the high voltage transformer in the microwave oven will be discussed in the later paragraph.

The potential health effects of styrene in vinylester resins on human beings are [8]:

- **Eye.** Exposure can cause eye irritation. Symptoms may include stinging, tearing, redness and swelling.
- **Skin.** Exposure can cause skin irritation. Prolonged or repeated exposure may dry the skin. Symptoms may include redness, burning, drying and cracking, skin burns and skin damage. Skin absorption is possible, but harmful effects are not expected from this route of exposure under normal conditions of handling and use.
- **Swallowing.** Swallowing small amount during normal handling is not likely to cause harmful effects; swallowing large amount may be harmful. This material

can enter the lungs during swallowing or vomiting. This result in lung inflammation and other lung injury.

- **Breathing.** Breathing of vapour or mist is possible. Breathing small amounts of this material during normal handling is not likely to cause harmful effects. Breathing large amounts may be harmful. Symptoms usually occur at air concentrations higher than the recommended exposure limits.
- **Symptoms.** Symptoms of exposure to this material through breathing, swallowing, and/or passage of the material through the skin may include: metallic taste, stomach or intestinal upset (nausea, vomiting, diarrhea), irritation (nose, throat, airways), central nervous system (CNS) depression (dizziness, drowsiness, weakness, fatigue, nausea, headache, unconsciousness) and other CNS effects, loss of coordination, confusion and liver damage.

The first aid measure for styrene in the resin will be [8]:

- **Eyes.** If symptoms develop, immediately move individual away from exposure and into fresh air. Flush eyes gently with water for at least 15 minutes while holding eyelids apart; seek immediate medical attention.
- **Skin.** Remove contaminated clothing. Flush exposed area with large amount of water. If skin is damaged, seek immediate medical attention. If skin is not damaged and symptoms persist, seek medical attention. Launder clothing before reuse.

- **Swallowing.** Seek medical attention. If an individual is drowsy or unconscious, do not give anything by mouth; place individual on the left side with a head down. Contact a physician, medical facility, or poison control centre for advice about whether to induce vomiting. If possible, do not leave individual unattended.
- **Inhalation.** If symptoms develop, move individual away from exposure and into fresh air. If symptoms persist, seek medical attention. If breathing is difficult, administer oxygen. Keep person warm and quiet; seek immediate medical attention.

The fire fighting measures for the material are [8]:

- **Flash point:** 26.6 – 32.2 °C
- **Explosive limit (for component):** Lower = 1.1 %, Upper = 6.1%.
- **Auto-ignition temperature:** No data.
- **Fire and explosion hazards:** Vapours are heavier than air and may travel along the ground or may be moved by ventilation and ignited by lights, other flames, sparks, heaters, smoking, electric motors, static discharge, or other ignition source locations distant from material handling point. Never use welding or cutting torch on or near drum (even empty) because product (even just residue) can ignite explosively.

- **Extinguishing media:** Regular foam, water fog, carbon dioxide and dry chemical.
- **Fire fighting instructions:** Wear a self-contained breathing apparatus with a full face piece operated in the positive pressure demand mode with appropriated turn-out gear and chemical resistant personal protective equipment. Polymerisation will take place under fire conditions. If polymerisation occurs in a closed container, there is possibility it will rupture violently.

Risks of MEKP

In addition to styrene, the organic peroxide initiators used are toxic and may be severe irritants and sensitisers to skin and eyes and may be corrosive if the concentration is high. The organic peroxides are also highly flammable and may decompose with explosive violence if not handled correctly. MEKP is a colourless solution of methyl ethyl ketone peroxide in dimethyl phthalate, with 9% active oxygen. MEKP should be stored in the original closed container in a cool place away from all sources of heat, sparks, or flames, and out of direct sunlight. Exposure to high temperatures or contamination with foreign materials may result in explosive decomposition. Do not store it in unvented glass containers. Do not store it in the vicinity of cobalt naphthenate, dimethyl aniline, or other promoters, accelerators, acids, bases, or strong reducing agents. Do not store it in the vicinity of food or drink. Do not reuse the container. Maximum storage temperature is 38 °C. Decomposition temperature is 68°C [9].

MEKP is a strong irritant. Avoid swallowing and all contact with eyes and skin. Ingestion can be fatal! Discard contaminated clothing. Wash contaminated skin

thoroughly with soap and water. If swallowed, take large quantities of milk or water and immediately call a physician. MEKP in the eye may result in irreversible blindness, even if flushed out with water! Flush the eyes immediately with water. Continue flushing for at least 30 minutes, and call a physician. Do not take chances with this chemical. Wear goggles, gloves, protective clothing, and a respirator, and be careful. Keep an “eyewash bottle” anywhere MEKP is used to provide instant first aid while one gets to a sink with running water [9].

It is necessary to ensure that all promoters and accelerators are thoroughly mixed into the resin before adding MEKP. These agents should never be mixed directly with MEKP. Violent decomposition and fire could result from such mixing or contamination. Stir MEKP into the resin slowly and carefully to avoid splashing. Spilled material should be absorbed in inert material such as vermiculite or sand and then wet with water. All such contaminated material should be placed in double polyethylene bags and kept out of doors and away from combustibles until it can be removed by qualified hazardous waste personnel. In case of fire, spray with water, preferably with a fog nozzle, or with carbon dioxide or foam from a safe distance. Dry chemical or other extinguishers may be effective against a very small fire [9].

In pouring MEKP to the vinylester resins, MEKP dispenser is recommended for use. The dispenser is adjustable to accurately dispense 2.5 to 35 cc. Squeeze the bottle until the upper vial is full then release pressure on the bottle leaving a precisely measured amount of catalyst in the vial. This is then poured out with no dripping. By doing this, the risk of contacting the chemical with skin is much reduced.

Risks of interaction of microwaves with vinyl ester resins

To achieve a bigger project objective, ie to reduce the shrinkage of vinylesters, it will be necessary to apply microwave energy in a multimode oven cavity to samples of particulate reinforced vinylester composites under controlled conditions. A commercial 1.8 kW microwave oven will be used for this purpose. The 1.8 kW power is actually achieved by launching microwaves from two 0.9-kW magnetrons. The power inputs can be varied from 10% (180 W) to 100% (1800 W) in steps of 180 W.

Whether a material will absorb microwave energy and convert it into heat depends on its relative complex permittivity and loss tangent. Ku et al. [10] showed that liquid rapid Araldite (epoxy resin) has a dielectric constant of 2.81 and a loss tangent of 0.244 at 2.45 GHz at room temperature. The loss tangent is quite high and it is expected that Araldite will absorb microwaves readily and convert it into heat. Vinylester resin is produced from modified epoxy resin and methacrylic acid (Peters, 1998); it is therefore expected that it will also absorb microwaves readily. A possible risk in applying microwave energy to the vinylester composite is the interaction of the vapourised styrene from the resin with the high voltage (HV) transformer in the oven. When the vaporised styrene is heated, it may flash but this did not happen in the experiments described later. Styrene is a highly flammable vapour and will be given off during the curing process of the composite. High vapour concentration of styrene may cause explosions but this did not occur in this study.

Some experiments were carried out to see the effects of microwaves on particulate reinforced vinylester composites. To start with a beaker of 10 millilitres of the

composite was exposed to microwave irradiation for 30 seconds. The power used was 180 W. There was no arcing at all. Longer exposures of 1 to 2 minutes of microwave irradiation were also tried for the same composite, again there was no arching. A beaker of 50 millilitres vinyl ester composite [VE/FLYASH (33%)] was then located in the cavity of the oven and a power level of 180 W was selected to cure the composite. The ambient temperature was 19 °C and relative humidity was 25%. Temperature was recorded every 1 minute of microwave irradiation. After one minute of exposing the composite to microwaves, the beaker was taken out and the temperature was measured. The temperature was 33 °C and there was no noticeable change in the composite. The composite was then re-located into the oven cavity and exposed to microwaves for another minute. It was found that the volume of the composite expanded dramatically (by about 15%) and the temperature was 80 °C. A drop (projection on top surface of a casting) with a hard crust floating on the uncured composite beneath was found. The surface finish was rough. It appeared that the increase in volume had been at the expense of the formation of voids in the composite. The crust was forced into the uncured composite, by a piece of small stick, which then covered most of it. The composite was then exposed to microwave irradiation for another 30 seconds. Temperature was found to be 119 °C and the whole composite was hard. It seemed that curing had completed. The volume increased a little bit further to 20% more than the original (50 millilitres). The surface was rough and irregular. After cutting the composite block through, it was found that voids appeared in the middle part of the block. It can be argued that the heat generated by microwave sped up the evolution of gases from the cast component and the volume increased [3].

In another occasion, a power level of 180 W and an exposure duration of 75 seconds, were selected to cure 50 millilitres of VE/FLYASH (33%) in a beaker. The ambient temperature was 24 °C and the relative humidity was 26%. The oven cavity temperature was 28 °C because the oven has been exposed to open space and under sunshine for 5 minutes. An ambient temperature of 28 °C should be used in carrying out analysis. After taking out the composite, its temperature was found to be 90 °C, which was 5 °C higher than the maximum temperature reached in curing 50 millilitres of the composite under an ambient conditions of 19 °C and relative humidity of 25% [3]. It was found that a drop with partially cured crust was formed. The volume of the drop was about 4 millilitres. The other part of the composites was not cured and was a rubbery solid. Forty five seconds later, the temperature was 135 °C and the composite became cured. At time equalled to 35 minutes, the temperature dropped back to 24 °C. After 24 hours, the height of the level of the composite in the beaker was measured and was found to be 31.22 mm. The original height was 29.09 mm. This results in an increase in volume by 10.2ml [3]. Adding the volume of the drop formed during curing, the total increase in volume was 14.2 ml. In this case, there was no shrinkage but an expansion in volume. The increase in volume was 28.4%. The resulting structure had a lot of spores and the strength of the composite was expected to be inferior.

The decision to microwave the composite for 75 seconds in the second trial has been made in accordance with the results obtained in the first trial. In the first trial, the temperature was 33 °C after the composite was exposed to microwaves for 60 seconds. It seemed that by exposing the composite to an extra 15 seconds to microwaves, the temperature would be raised to around 10-20 degrees above the

ambient temperature. This was wrong, the temperature after exposing the composite to microwaves for 75 seconds was 90 °C, which was 5 °C above the peak temperature for curing the composite in ambient conditions. This is due to the difference in ambient temperature and relative humidity in two occasions. They are 9 °C (oven cavity temperature) and 7 % higher in temperature and relative humidity in the microwave cured conditions than in ambient conditions respectively. With the ambient conditions of the second trial, the microwave exposure time should be 40 seconds or less. This may result in an increase in temperature of 10 –20 degrees Celsius. A drop formation could also be avoided. The composite was then cured under ambient conditions.

In the third trial, the ambient conditions were the same as in the second trial. The power input was 180 W and the time of exposure to microwaves was 30 second. After taking out the composite, its temperature was found to be 44 °C, which was still far away from the maximum temperature in the second case. There was no drop formation but there was an expansion in volume. At time equalled to 9 minutes, a peak temperature of 137 °C was attained and the volume was 54.74 ml, an increase of 2.32 % from 53.5 ml. The composite was also cured. At time equalled to 40 minutes, the temperature returned to 24 °C. After 24 hours, the volume of the composite was measured and was 52.27 ml. The percentage of shrinkage was 2.30 % and the steps of calculations are given below [11]:

Initial volume = 53.5 mm³.

Initial height level in beaker = 30.89 mm.

Final height level in beaker = 31.13 mm.

The linear shrinkage of the composite = 31.13 – 30.89 = 0.24 (mm)

The volumetric shrinkage of the composite can be expressed as [12]:

$$V_{\text{cured}} = V_{\text{uncured}} \times \left(1 - \frac{\Delta L}{L_0}\right)^3$$

$$\begin{aligned} \text{Therefore, } V_{\text{cured}} &= 53.5 \text{ ml} \left(1 - \frac{0.24}{31.13}\right)^3 \\ &= 53.5 (0.9923)^3 = 53.5 (0.977) = 52.27 \text{ ml.} \end{aligned}$$

$$\text{The shrinkage is } \frac{53.5\text{ml} - 52.27\text{ml}}{53.5\text{ml}} \times 100\% = 2.30\% .$$

Larger volumes, each 200 millilitres, of the composite, VE/FLYASH (33%), were also exposed to microwave irradiation for 30, 35 and 40 seconds respectively. No abnormal phenomenon was observed in each of the case. They were then allowed to cure in ambient conditions. The temperatures of the samples rose to 143, 144 and 145 °C respectively. The volume shrinkage in each case was nearly negligible. The process of curing larger volume of the composite seemed to be safe. More details about the experiments are tabled in Table 2 [13].

To make a volume of 200 millilitres of uncured composite (of 44% by volume of flyash or of 33% by weight), the total volume of resin plus hardener = 200 millilitres x 0.56 = 112 millilitres. For a composite with 98% resin and 2% hardener by volume, the volume of resin required = 112 millilitres x 0.98 = 109.8 millilitres and that of hardener required is 2.2 millilitres. It is easier to measure mass rather than volume so 109.8 millilitres of resin is converted to 109.8 x 1.1 = 120.8 g of resin, where 1.1 is the relative density of the resin. The mass of the styrene in the resin is therefore = $\frac{120.8\text{g}}{2} = 60.4 \text{ g}$ as the resin used contains 50% by weight of styrene. The

chemical formula for styrene is $C_2H_3C_5H_6$; its molecular weight is $12 \times 7 + 1 \times 9 = 93$. If one mole of styrene evaporates under (stp) standard temperature (zero degree Celsius) and pressure (760 mm mercury) condition. Its volume will be 22.4 litres or 22400 cc (cm^3) [14]. Therefore, if all the styrene in the resin (50% by weight) evaporates, its volume will be $\frac{60.4}{93} \times 22400 \text{ cc} = 14548 \text{ cc}$. This will never happen

because not all the styrene will evaporate instantly at standard temperature and pressure (std) and occupies nearly the entire oven cavity (17820 cm^3). The styrene vapour concentration in the oven cavity should not be very high because no flashing (flashing point is $26.6 \text{ }^\circ\text{C}$ to $32.2 \text{ }^\circ\text{C}$) of the chemical happened even when it was heated to $52 \text{ }^\circ\text{C}$, a temperature attained when 200 ml of the vinylester composite was heated by exposing it to microwaves at a power level of 180 W for 40 seconds. Moreover, explosion of the styrene vapour also did not take place; this implies that the concentration of it in the cavity was below the threshold value for explosion to occur [13].

The cavity of the oven is $30 \text{ cm} \times 33 \text{ cm} \times 18 \text{ cm} = 17820 \text{ cm}^3$ and the lower explosive limit for styrene (for component) is 1.1 % [8]. Therefore, the styrene vapour concentration in the cavity will be less than $17820 \text{ cc} \times 1.1\% = 196 \text{ cc}$ at any instant as there was no flashing and explosion. Experiments showed that the air in the cavity was forced out of the cavity through one of the vents at the back of the facility when the oven was in standby mode. The oven does not have an exhaust fan. A blower motor or fan (see Figure 4) inside sucks air through the air filter at the front and cools the HV transformer as the air passes. The air from the fan is blown into a duct and cools the magnetrons, which are located below the letter 'M' in Figure 5. One magnetron is at the top and the other is at the bottom. The heated exhaust air

leaves the oven through the upper and lower exhaust outlet as shown in Figure 6. The ventilation system seems to be efficient enough to keep the HV transformer cool. Some air is forced into the cavity at the back and then force out of the oven via the upper exhaust outlet at the back (see Figure 6). The airflow from the upper exhaust outlet is expected to be higher than that from the lower outlet because the upper outlet combines the exhaust air for cooling the upper magnetron and the exhaust gas from inside the oven cavity. On the other hand, the lower exhaust outlet only allows the exit of exhaust air for cooling the lower magnetron. An airflow meter was used to measure the airflow from the upper as well as the lower exhaust outlets. It was found that the airflow from the upper exhaust outlet was 2.3 metres per second and that from the lower outlet was 1.7 metres per second. The airflow rates are the same whether the oven is in operation with load inside the cavity or when the oven is in standby mode.

The exhaust gas from the oven cavity contains a small amount of styrene vapour, it is therefore a possible source of risk. The styrene vapour may be heated up by the heated HV transformer as it passes through the latter and may lead to flashing or explosion. A modification of the oven is therefore required to avoid this risk. From Figure 6, it is found that the exhaust air from the cavity re-joins the air for cooling the upper magnetron, near the letter 'M', through a bend. The modified design is to have the bend sealed and re-direct the air from the cavity, by means of a fan, to somewhere far away from the HV transformer via a duct of 5 metres long or more. The additional fan speeds up the discharge of the styrene vapour into a safe location. The modified oven and its peripherals are shown in Figure 7. An airflow meter was again used to measure the airflow from the upper as well as the lower exhaust outlets. It was found

that the airflow from both exhaust outlets was 1.7 metres per second. This means that all the exhaust air from the oven cavity has been re-directed to somewhere it is safe to dispose it.

It can be argued that the cavity size and power of the microwave oven used in this study is by far too small and low for curing vinylester composite components used in industry. It is unlikely that an oven with a cavity size, say, 1 m x 1m x 1m, required to accommodate most sizes of industrial vinylester composite components, is readily available in the market. The solution is to design and tailor-made a microwave oven with the required cavity size and power. Meredith [15] outlined the criteria for designing the oven cavity.

Conclusion

The paper describes the risks posed by styrene vapour, MEKP, the interaction microwaves with the styrene vapour and the design of the oven in curing vinylester resins using microwaves energy. All possible risks brought about by the above items were discussed in detail together with the ways of avoiding accidents. From the preliminary studies, it was found that explosion of the styrene vapour would not happen provided the resin was not heated for too long. With a power level of 180 W, the duration of microwave exposure should not exceed 40 seconds. The ventilation system inside the cavity must also be very good.

With the modified oven, the authors will endeavour to perform more experiments on microwaving the vinylester composites so that more useful and relevant information

can be disseminated to the public in the near future. The suggestions made by this paper are not exclusive and researches still need to be careful in carrying out the experiments.

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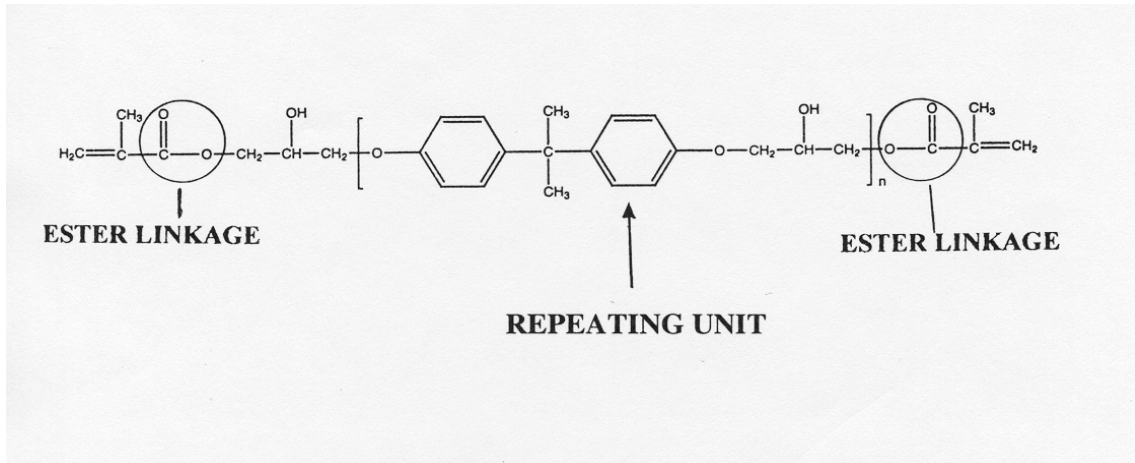
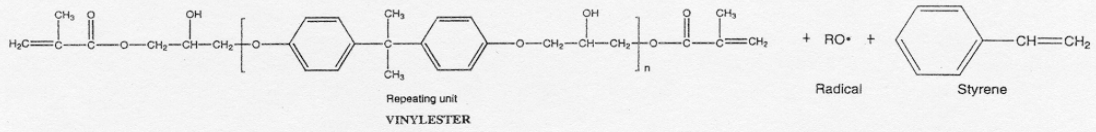
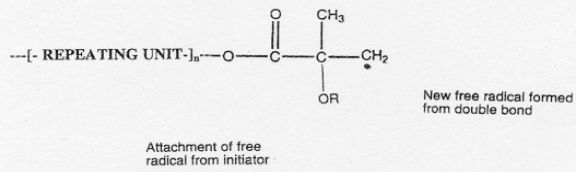


Figure 1: The structure of bisphenol A vinyl ester

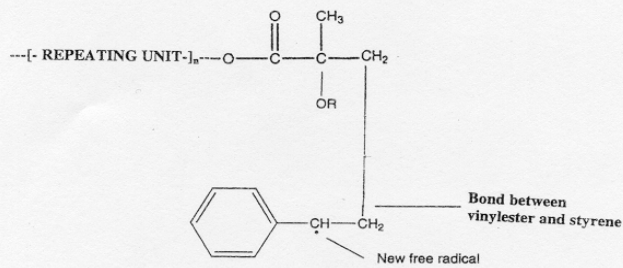
REACTANTS



INITIATION STEP



BRIDGING STEP



CROSSLINKED POLYMERS

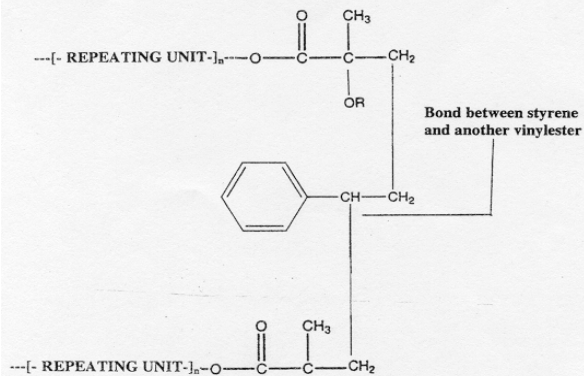


Figure 2: Schematic of addition or free radical crosslinking of vinyl ester

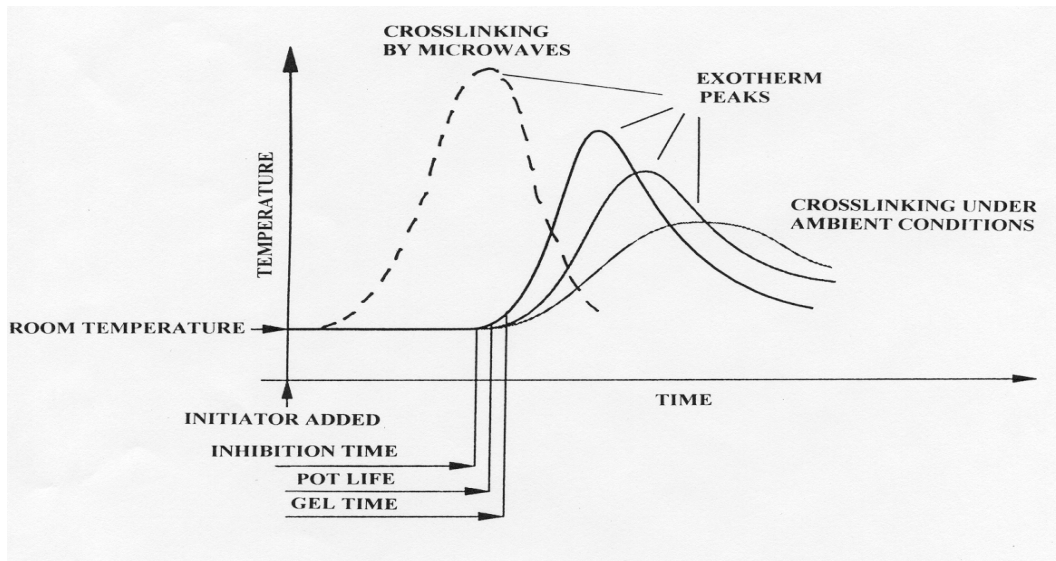


Figure 3: Temperature time relationships for crosslinking of vinyl ester

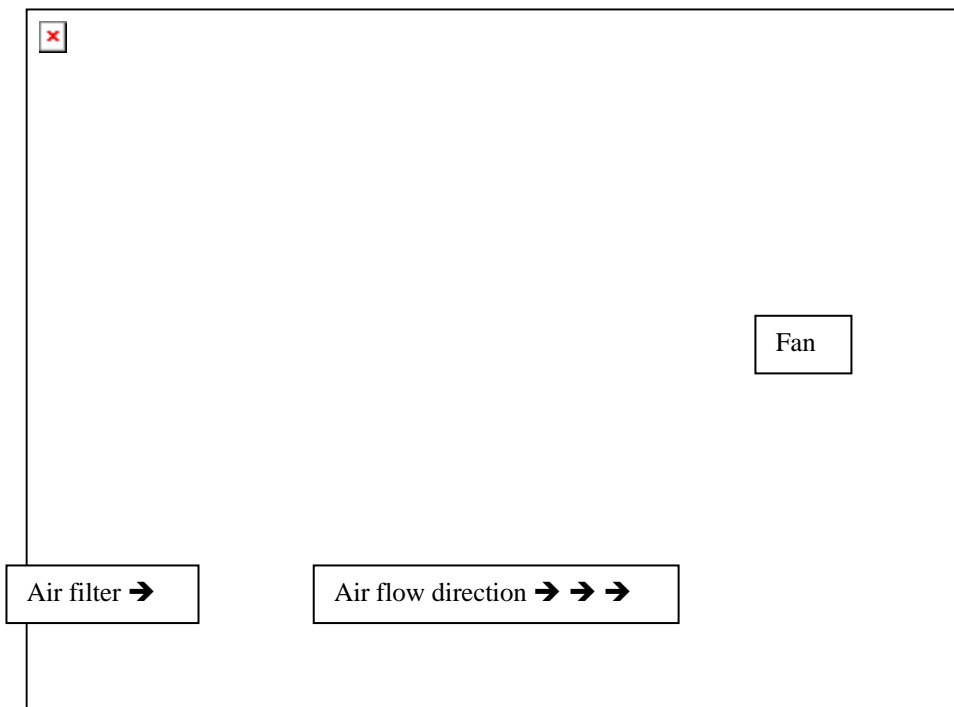


Figure 4: The side view of the (sectioned) microwave oven

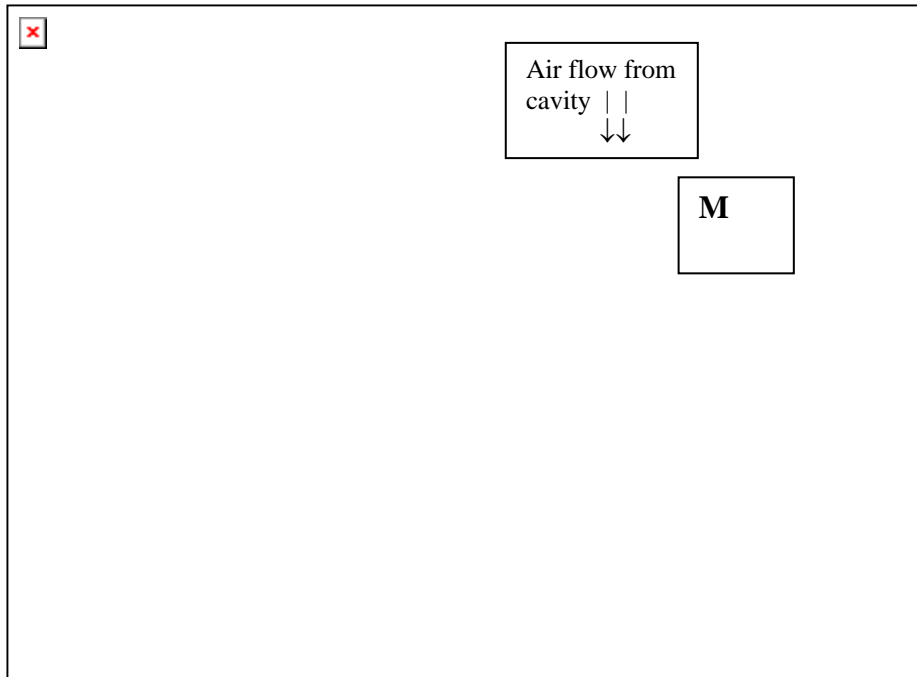


Figure 5: The plan view of the microwave oven

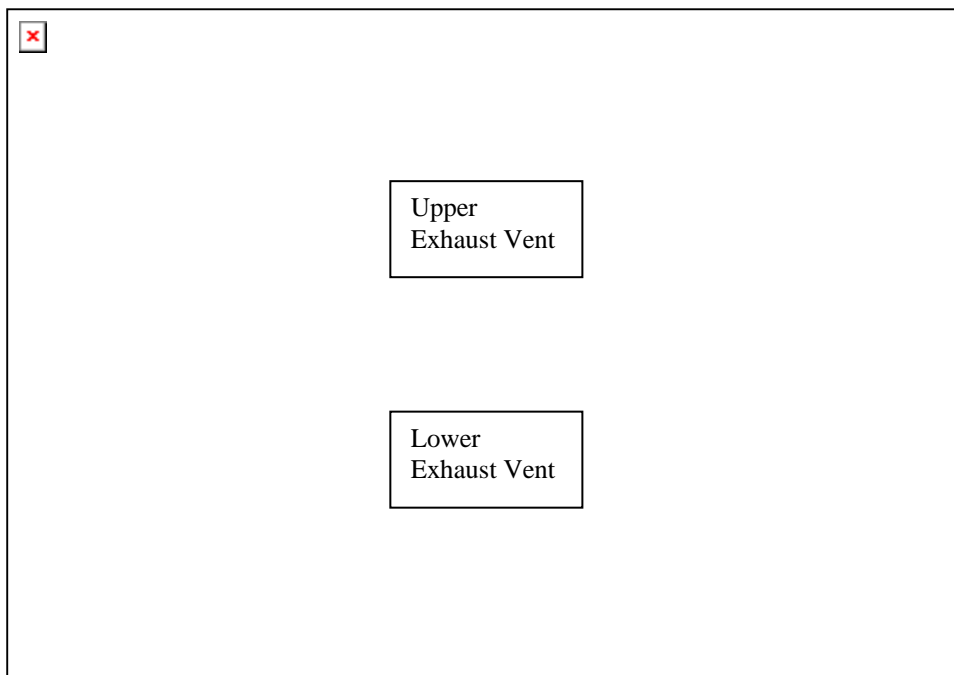


Figure 6: The back view of the microwave oven

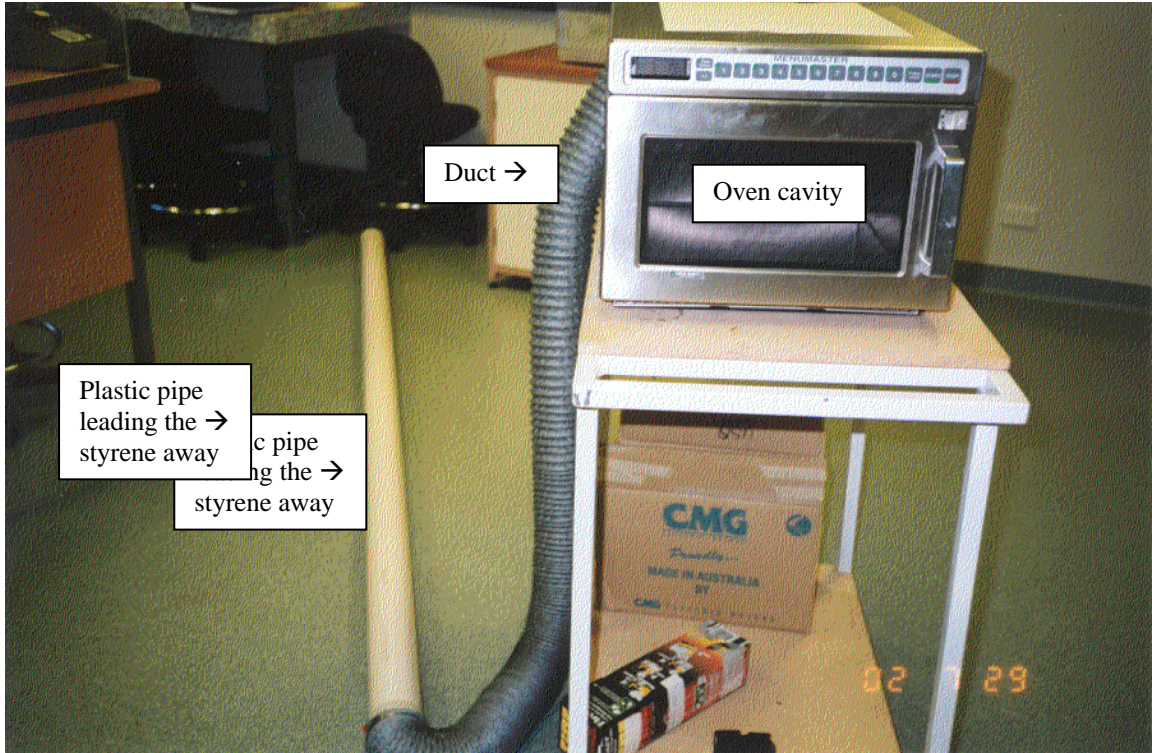


Figure 7: The modified oven and its peripherals

Table 1: Permissible Emission Limits (PELs) for styrene in different English speaking countries

Countries	TWA (ppm)	STEL (ppm)
Australia	50	100 (15 min)
Canada	50	100 (15 min)
South Africa	50	NA
UK	100	250 (10 min)
USA	50	100 (15 min)

Table 2: Volume shrinkage and other parameters for 200 ml of VE/FLYASH (33%) exposed to 180-W microwaves at different duration

Microwave exposure time (seconds)	0	30	35	40
Oven cavity Temperature (°C)	20	28	25	25
Temperature after microwave exposure	NA	41	45	52
Original volume (ml)	200	200	200	200
Final volume (ml)	47.36	202.32	199.36	200.06
Volume shrinkage (%)	6.4	1.16	0.32	-0.03
Volume at maximum temperature (ml)	187.22	204.64	201.28	201.00
Time to reach gel time (minutes)	32.5	3	1	1
Maximum temperature	117	143	144	145
Time to reach maximum temperature (minutes)	37.5	9	6	6