

**EGE UNIVERSITY GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

(MASTER THESIS)

**STUDIES ON THE RECYCLING OF GLASS FIBER
REINFORCED POLYESTER RESIN COMPOSITE**

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Discipline Code: 603.03.00
Presentation Date: 18.10.2009

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Gülden KUTLUATA tarafından Yüksek Lisans tezi olarak sunulan “Studies on the Recycling of Glass Fiber Reinforced Polyester Resin Composites” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET**CAM ELYAF TAKVİYELİ POLYESTER REÇİNELİ
KOMPOZİT MALZEMELERİN GERİ DÖNÜŞÜMÜ ÜZERİNE
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Tez Yöneticisi: Prof. Dr. Mesut YENİGÜL

Kasım 2009, 51 sayfa

Bu tezin amacı, cam elyaf takviyeli polyester (CTP) geri dönüşümü sağlayacak çalışmaları gerçekleştirmektir. CTP kompozit atıklarının yeni ürünler haline getirmek için geri dönüşümü çalışılmıştır. Mekanik geri dönüşüm tekniği, atık kompoziti öğütme ve boyutsal sınıflandırma işlemlerini içerir. Burada boyutsal sınıflandırılmış CTP'nin, dolgu malzemesi olarak yeni kompozit hazırlanmasında tekrar kullanımı amaçlanır. Isıl geri dönüşüm prosesi ise atık kompoziti enerji değerinden faydalanmak için yakma işlemidir.

Atık CTP tozunun, kalsit ile karşılaştırılarak dolgu malzemesi olarak kullanılabilirliği çalışıldı. Deneyler süresince alınan örneklerde, elastik modülü ve bükülme dayanımı testleri gerçekleştirildi. Ayrıca, sertleşme sıcaklığı, jelleşme ve sertleşme zamanlarını içeren ısıl testlerden de faydalanıldı. Isıl testlerde dolgu malzemesi kullanıldığında gerek kalsit gerek atık CTP tozu birbirine yakın sonuçlar vermiştir..

Öğütülerek elde edilen CTP tozları dolgu malzemesi olarak tekrar kompozit yapımında kullanılabilir. Kalsit dolgu malzemesi yerine atık toz CTP kullanabileceğimiz bu çalışmada görüldü.

Anahtar kelimeler: cam elyaf takviyeli polyester, , kompozit geri dönüşümü, geri kazandırılmış cam elyaf, polimer kompozit malzemeler, atık geri dönüşümü

ABSTRACT
**STUDIES ON THE RECYCLING OF GLASS FIBER REINFORCED
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MSc in CHEMICAL ENG.

Supervisor: Prof. Dr. Mesut YENİGL
November 2009, 51 pages

The aim of this thesis is investigating reuse of glass fiber reinforced polyester composites (GRP) into new composites. This composite recycling waste were studied into new products. Mechanical recycling technique includes waste grinding and dimensional classification processes. Here, classified GRP is intended to reuse as a filling material to the virgin mix. Thermal recycling process is an incineration process which uses the combustion energy of the waste material.

GRP waste dust was used instead of calcite filler for the comparison of the mechanical and thermal properties. The prepared samples were tested for tensile and flexural strengths and corresponding moduli and bending strengths were found. In addition to mechanical tests, thermal behaviour including peak temperature, gel and peak of time were found. When the filling material was used in the thermal test both calcite and waste GRP dust gave results close to each other.

The ground GRP waste dust can be used as filling material in new composite products. In this study, it can be concluded that GRP waste dust could be used instead of calcite as a filling material.

Keywords: glass fiber reinforced polyester, composite recycling, glass fiber recycle, polymer composite materials, waste minimization, waste recycling, recycled composite

ACKNOWLEDGEMENT

I would you like to thank my supervisor Prof. Dr. Mesut YENİGÜL for his valuable advise, all kinds of helps, great patience and special interest during my master of science thesis.

I should give my special thanks to Erdem YÜCEL and Erdal YÜCEL from FIBROSAN GROUP Inc. for inviting me to their laboratory and for their special interest. I am also grateful to chemist Duygu ÖLMEZ for her support in the experiments.

I should say a special thank to Prof. Dr. Sevgi ULUTAN for her valuable advise and special interest for the course of research.

I would like to thank my parents Kibriye KUTLUATA and Adnan KUTLUATA for their support and encouragement for my education. I should extend my thank to my brother Uğur A. KUTLUATA and my sister Gülen KUTLUATA GENCER for their motivation during the my master of science thesis.

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NOMENCLATURE

| | |
|-------|---|
| BZA | : Benzly Alcohol |
| DGMM | : Diethyleneglycol Monomethylether |
| DMC | : Dough Moulding Compound |
| ECRC | : European Composites Recycling Concept |
| DTG | : Derivative Thermogram |
| GRP | : Glass fiber reinforced Polyester |
| GPRMC | : European Composites Industry Association |
| GF | : Glass fiber |
| FRP | : Fiber reinforced polyester |
| MEK | : Methyl Ethyl Ketone |
| TG | : Thermogram |
| PET | : Polethylene Terephthalate |
| UPR | : Unsaturated polyester resin |
| UP | : Unsaturated polyester |
| UV | : Ultraviolet |
| WEEE | : Waste electrical and electronic equipment |

1. INTRODUCTION

The glass fiber reinforced polyester (GRP) is one of the most difficult materials to separate into its elemental components, namely fiber, filler, and polymers in the waste recycling process. Therefore, the wastes are treated in the incineration or landfilling without any recycling approaches.

The fibrous recyclates have some potential as reinforcement materials, but they are not as good as the virgin reinforcement, and there are problems associated with the bonding of the recyclate with polymers and the tendency for the larger pieces of recyclate to be stress raisers and act as failure initiation sites (Kouparitsas, 2003). The thermal recycling processes have the advantage of being able to tolerate more contaminated scrap materials. The fluidised bed process produces a very clean fibre product, but it is not in the same form as an existing virgin fibre products. Development work is therefore needed to identify the ways in which the material can be reprocessed into cost effective new products. The same is also true of the fibre products developed from the pyrolysis processes.

These may have varying degrees of char on the recycled fibres, which may limit the reuse options or require further processing to remove it. The pyrolysis processes are generally more complex in principle than the fluidised bed process but do produce potentially useful organic products from the polymer.

Applications of composite usage are wide-ranging. Some applications include: car body panels, car bumper beams, heat shields, show, stadium seating, and circuit boards.

Polyester resins are combined with short glass fibres and low cost fillers to produce moulding compounds for applications where high mechanical properties are not required. GRP is a very convenient material for the prefabrication of bathroom units and components. Composite made by press moulding is used in the fabrication of cold and hot water storage tanks. When the matrix is made from a special type of polyester resin, thorough testing has shown that the tank can

withstand working levels of pressure and temperature. GRP composite is also used in the fabrication of window frames and concrete formwork.

Mechanical recycling or other forms of thermal recycling mean that the recyclates currently produced are too expensive to give a clear market advantage over alternative existing materials. Furthermore, commercially viable operations require large throughputs and markets need to be developed to consume these quantities of recyclate. Either the recyclates must find higher value end markets and this may mean developing new higher grade recyclates or the cost of the recyclate must reduce to allow the recyclates to penetrate further into existing markets. A recent study investigating recycling routes for scrap thermoset composites from the construction industry has reported that significant incomes could be earned if recyclates were used as filler materials replacing woodchip or recycled plastics. However, it was also noted that the difficulty of using the recyclates in processes already optimised for existing products was a barrier. The future therefore lies in developing markets into which the recycled products can be sold at profitable prices and some ongoing studies are focussing on this aspect (Pickering, 2006). Glass fibre composites comprise the bulk of the thermoset composites currently manufactured.

In Europe, approximately 1 million tonnes of composites are manufactured each year. Although, there are many successful uses for thermoset composite materials, recycling at the end of the life cycle is a more difficult issue. However, the perceived lack of recyclability is now increasingly important and seen as a key barrier to the development or even continued use of composite materials in some markets.

European Composites Recycling Concept (ECRC) has been focusing on the development of recycling solutions composite systems, mainly consisting of thermoset polyester resin and glass fibre. In Germany, GRP wastes have been banned to dispose them into landfill, due to their high (30%) organics content (Larsen, 2009).

Although the hierarchy of waste management routes appears to give preference to those recycling routes that maximise material recovery, the mechanical recycling of valuable fibres and resins as fillers does not necessarily give the best environmental return. Pyrolysis process has the potential to produce chemical feedstocks from the polymer but these may be difficult to refine from the mixture of products produced. If a pyrolysis process only produces chemicals suitable for use as fuels then an energy recovery process with high quality fibre recovery may be more acceptable.

Only environmental controls of the recycling routes can identify which are the most acceptable and although some work has been studied much more analysis of the recycling processes needs to be done. GRP composite materials are used in a wide range of applications in industries such as automotive and construction industry. Depending on formulation and use, they may be fabricated into products that are light in weight, transparent, translucent or opaque, colourless or coloured, flat or shaped sheets, with no limit to the size of object that can be made. They come in a variety of forms. Mechanical recycling processes are suitable for scrap composite material which is relatively clean and uncontaminated and from known origin. The technologies developed produce powder and fibrous recyclates, which have potential for reuse. However, the dust recyclates have limited potential for reuse into the thermoset compounds from which they originated. Although they are of lower density, there are other drawbacks to their use in terms of ease of processing and lower mechanical properties in the products in which they are used. Currently, regrinding method is the only commercially applied method.

1.1 The Aim of the Study

The objective of this study is to investigate a recycling technology that will enable the Glass Fiber Reinforced Polyester Industry to recycle its glass fiber reinforced polyester (GRP) into new composite products.

The results we obtained with the instruments of Flexural and Testo Exotherm devices provided an important scientific knowledge about the quality

parameters of the recycled composite. The change in composite properties with respect to the changing weight percentages of waste GRP determined by tensile, flexural, gelation time, peak temperature and peak time values will be investigated by using, mechanical, thermal, etc. testing and analyzing methods.

Reusing plastic is preferable to recycling as it consumes lesser amounts of energy and resources.

1.2 General Information and Literature Analysis

1.2.1 Properties of Glass Fiber Reinforced Polyester Composites

Pickering, 2006 stated that the properties of the finished GRP composite material depend on a great number of compositional and fabrication factors, some of the most important being resin formulation, filler, curing conditions, type and amount of reinforcement, coupling agent (bonds the resin to the glass), fabrication process and workmanship.

Kouparitsas et al, 2002 noted that by choice of ingredients, special properties can be achieved. For example, fire retardance can be imparted by incorporating appropriate additives. Although it is preferable to modify the basic unsaturated polyester resin to provide built-in fire resistance; weathering resistance can be enhanced by the use of neopentyl glycol and methyl methacrylate; and thermoplastic polymers can be added to reduce shrinkage during curing. GRP reinforced with chopped strand mat is essentially isotropic, whereas cloth fabric reinforcement and roving give a material that is an isotropic in character, with properties varying directionally.

Because of the great number of factors that define a GRP composite, the range of mechanical and other physical properties is very wide. For example, tensile strength at room temperature may vary from 69 MPa (10^4 psi) to 896 MPa (13×10^4 psi) or higher, wet strength retention (material saturated with water) from 50 to 95 per cent, and specific gravity from 1.2 to 1.9. The range of some physical properties given in Table 1.1 is typical for GRP sheet materials produced

with normal care from general purpose polyester resin and reinforced with three types of glass-fibre reinforcement.

Physical properties of glass-fibre reinforced general purpose polyester sheet for reinforced with various glass-fibre construction is seen in Table 1.1, Kouparitsas et al, 2002.

Table 1.1 Physical properties of glass-fibre reinforced general-purpose polyester sheet (reinforced with various glass-fibre construction) (Kouparitsas et al, 2002)

| Property* | Chopped-Strand Mat or Premix** | Type of Reinforcement Parallel Roving | Chopped-Strand Mat or Premix**143*** Fabric Parallel Laminated |
|---|---------------------------------------|--|---|
| Glass content, weight % | 25-45 | 50-70 | 62-67 |
| Specific gravity | 1.4-1.6 | 1.7-1.9 | 1.7-1.9 |
| Tensile strength, MPa (10 ³ psi) | 76-160 (11-23) | 550-900 (80-130) | 540-600 (78-87) |
| Tensile modulus, MPa (10 ⁶ psi) | 5.6-12 (0.82-1.8) | — | 31 (4.5) |
| Flexural strength, MPa (10 ³ psi) | 140-260 (20-38) | 690-1400 (100-200) | 590-720 (85-105) |
| Flexural modulus, GPa (10 ⁶ psi) | 6.9-14 (1.0-2.0) | 34-49 (5.0-7.0) | 31-38 (4.5-5.5) |
| Compressive strength, MPa (10 ³ psi) | 120-180 (18-26) | 340-480 (50-70) | 280-340 (40-50) |

* Resistance to continuous heat: 150-205°C (300-400°F); heat deflection temperature (as tested by ASTM Method D648) under a stress of 1.82 MPa (264 psi): 190-260°C (375-500°F); coefficient of linear expansion, 10⁻⁶/°C: 11-36 or 10⁻⁶/°F:6.0-20.0.

** Putty-like mixture consisting of resin, chopped fibres, fillers, activator and other ingredients, ready for moulding.*** Code for a weave style of glass-fibre fabric, 0.23 mm (0.009 in) thick

1.2.2 Orthophthalic Unsaturated Polyester Resin for General Purpose Applications

An unsaturated polyester resin contains a number of C=C double bonds. A condensation reaction between a glycol (ethylene, propylene, or diethylene glycol) and an unsaturated dibasic acid (maleic or fumaric) gives unsaturated polyester resins (UP), Chawla, 1998. Mechanical properties of cured unsaturated polyester are seen in Table 1.3 and Table 1.4.

Table 1.2 Chemical properties of unsaturated polyester (CE 92 N8)

| PROPERTIES | UNIT | SPECIFIC VALUES |
|-----------------------|---------|-----------------|
| Appearance -- | Clear | |
| Viscosity at 25°C | Cps | 400 ± 60 |
| Acid Number | mgKOH/g | Max 25 |
| Solid content | % w/w | Min 58 |
| Gel-time(*) | Minutes | 8 ± 2 |
| Exotherm peak(*) | °C | 180 ± 20 |
| Stability in the dark | Months | 4 |

(*)Gel-time and exotherm peak are measured with a 100 g sample of resin in a beaker of 50mm diameter at 25 °C with 2 g. of 50 % activated Methyl Ethyl Ketone Peroxide and 0.25 g. of 6 % solution of Cobalt Naphtanate. (www.poliya.com).

Table 1.3. Mechanical properties of cured unsaturated polyester (CE 92 N8)

| Properties | Unit | Specific Values |
|-------------------|--------|-----------------|
| Hardness | Barcol | Min.42 |
| Flexural strength | MPa | Min.900 |
| Tensile strength | MPa | Min.500 |

1.2.3 Fillers

GRP waste can be used as fillers with virgin resins or other materials like concretes or as filler material in road construction. In such applications, chemical composition of the plastics is generally not very significant. This is an easy way to recycle thermosets or contaminated plastics in second grade applications. One such use is thermoplastic wastes that are melted and coextruded or co-injected into mouldings with virgin resins. These virgin resins with superior properties are forced into the perimeter of the mold while the recycled plastics, with inferior properties, are injected in the center of the mold (Curlee, 1986). Plastic wastes may also be used with some effectiveness as a partial replacement of inorganic aggregates in concrete applications to decrease the dead weight of structures. Similarly, recycled rubber can be used in asphaltic concrete mixes (McQuillen et al., 1998) or as a fill material in road construction (Eldin and Senouci, 1992).

The advantages of adding recycled rubber to the asphalt mix include increased skid resistance under icy conditions, improved flexibility and crack resistance, and reduced traffic noise. Many researchers have reported the use of scrap tire/rubber in cement mortar and concrete, and Siddique and Naik (2004) have published a review paper, detailing the research on the use of scrap tire/rubber in concrete. Remias et al. (2000) developed a system which utilizes nitrogen oxides and dioxygen to break down and oxidize polyethene. The principal nongaseous products were acids, mainly succinic, glutaric, adipic and pimelic acids. Ernst et al. (2000) used electrochemical applications for quantification of heavy metals for the recycling of waste plastics.

Masuda et al. (2001) developed a new reactor system for recovery fuels from the waste plastic mixture in steam atmosphere. This system was composed of three kinds of reactors connected in series. One was a reactor filled with stirred heat medium particles, which enabled the high heat transfer rate, the high holdup and the good contact of the melted plastics with steam. The second was a tank reactor. The last one was a fixed bed reactor with FeOH activator particles, which showed the catalysis in steam for the decomposition both of a wax and sublimate materials generated by the degradation of plastics.

Cavalieri and Padella (2002) reported that a polymer milling process with liquid CO₂ was applied to polymeric mixed waste, obtaining a powder material which was successfully utilized as a matrix for a new composite material. Developed materials have interesting mechanical properties, and material performance can easily be improved. Investigations on selected mixtures of PP and PE clearly showed evidence of chemical compatibilization.

Miskolczi et al., 2004 reported that fuel-like utilization is one way of chemical recycling of liquids from waste polymers. Hall and Williams (2007) investigated three plastic fractions from a commercial waste electrical and electronic equipment (WEEE) processing plant for the possibility of recycling them by batch pyrolysis.

1.2.4 GRP Applications in Construction

GRP composites used in construction can be divided into two main classes: the standard items of manufacture such as single-skin sheet (flat and corrugated) or sandwich panels, and the custom structures designed for a specific application by an architect or engineer. Details of the manufacturing processes, properties and structural capabilities for standard products have been established. Regarding the use of custom-tailored structures, the building designer should consider the basic characteristics, behaviour of the material, and the manufacturing processes when selecting the appropriate material for a particular application (Blaga, 1978).

As seen in Figure 1.1 industrial commercially products are made by GRP in Fibrosan Inc., Izmir, Turkiye.



Figure 1.1 Industrial products made by GRP (photo courtesy of Erdem Yucel, Fibrosan Inc., Izmir, Turkiye)

Light-transmitting panels

Because of their relatively high light transmission (about 85 %), light weight, toughness and, where appropriate, fire retardancy, transparent and translucent GRP panels (usually corrugated) have a variety of uses including glazing for skylights, luminous ceiling or roofing, inner partitions and canopies.

Opaque and sandwich panels

GRP sheet material is used as cladding on other structural materials or as an integral part of either a structural or a non-loadbearing wall panel. In the former it functions as a decorative cladding (non-loadbearing) on concrete or brick, providing a wide range of coloured and textured surfaces. The GRP sheet used is usually opaque, but it may be translucent or transparent.

As an integral part of either a structural or non-loadbearing panel, opaque GRP can be used in a variety of ways. It is invariably the exterior skin. The most popular panel is the sandwich type, with an inner and outer skin of GRP and a

foam core of polyvinyl chloride (PVC), polystyrene, polyurethane or phenolic plastic. Another application for foam-cored GRP-faced sandwich panels is as wall panels in mobile homes and in boat hulls.

GRP composite in sectional and modular units

In addition to lightness, ease of fabrication of large components and simplicity of jointing make GRP composite materials particularly suitable for use in modular construction. Building components or sections are prefabricated and can be rapidly assembled on the building site. This makes them particularly suitable where access is limited or where ground cannot support traditional structures without excessive cost for foundations. Examples include living accommodation and laboratories at Antarctic bases, lighthouse towers, desert accommodation, and living accommodation on off-shore drilling rigs. The walls of sections or modules usually consist of a GRP sandwich panel with a plastic foam or honeycomb core.

Miscellaneous applications

GRP is a very convenient material for the prefabrication of bathroom units and components. Composite made by press moulding is used in the fabrication of cold and hot water storage tanks. When the matrix is made from a special type of polyester resin, thorough testing has shown that the tank can withstand working levels of pressure and temperature. GRP composite is also used in the fabrication of window frames and concrete formwork.

1.2.5 Durability of GRP Composites

According to durability of glass-fiber/polymer composites is dictated by the durability of the components: glass fiber, polymer matrix, and the interface. Environmental attack by moisture, for example, can degrade the strength of the glass fiber; plasticize, swell, or microcrack the resin; and degrade the fiber/ matrix interface by either chemical or mechanical attack.

The relative rates of these degradation processes are a function of the chemistry of the resin, temperature, length of time of exposure, degree of stress (whether cyclic or static), chemistry and morphology of coating of coupling agent on the GF, and type of GF. Several examples illustrate how the chemistry and morphology of the coatings of coupling agents that are on the glass fiber influence the strength and durability of the interfacial region.

Blaga (1978), Although considerable progress has been made in improving the durability of GRP composites, commercial products of these materials still deteriorate outdoors. Deterioration usually starts at the outer surface, its rate depending on the composition of the material, manufacturing method, degree of cure, nature of surface finish and service environment. Recent studies of sheet GRP materials at DBR/NRC have demonstrated that there are two main types of surface deterioration: breakdown in the glass-resin interface resulting in fibre pop-out, and surface microcracking of the matrix (Figure 1.2 and Figure 1.3). Both affect the appearance of the GRP sheet and its light transmission. If surface deterioration is severe, mechanical and other properties also suffer. Other changes occurring with outdoor exposure are discoloration and surface pitting, which can affect the physical properties of the sheet.

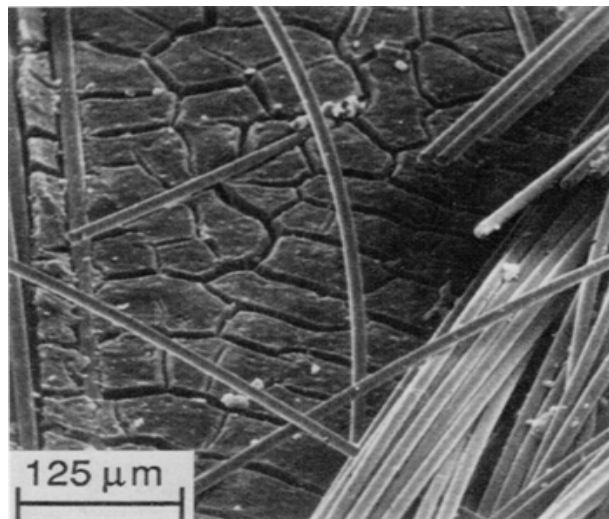


Figure 1.2. Surface of GRP (top side) weather outdoors for 12 years. (Blaga, 1978)

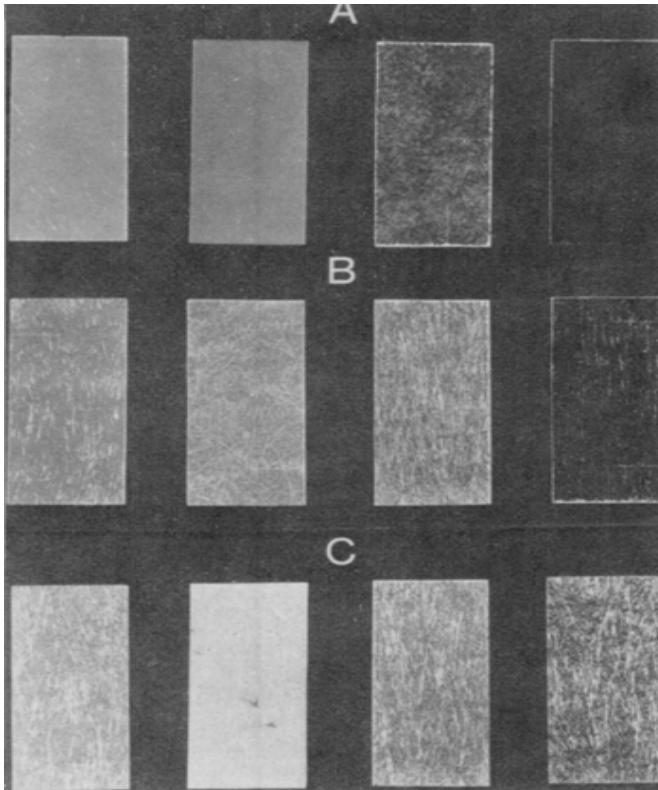


Figure 1.3. Different coloured flat sheets (aqua-marine, yellow, colourless, green) weathered for 5 years. A) control B) under side C) upper side (original size of sheets 21.5 x 9.5 cm) (Blaga, 1978)

Fibre pop-out develops under the influence of environmentally induced (thermally or by moisture) stress-fatigue, which causes gradual fracture and spalling of the resin surrounding the glass. Figure 1.3. shows that weathering studies indicate that fibre prominence could be extensive in conventional GRP sheet after a relatively short period (five years) of exposure in the Canadian climate . There was considerably less fibre pop-out on the under side of a panel even after eight years of outdoor exposure. This is understandable because the exposure conditions prevailing on the unexposed side are less severe, Blaga (1978).

Surface microcracking, the other type of breakdown, generally occurs on the side of the sheet exposed to solar radiation after fibre pop-out has become relatively extensive. It takes place under the combined action of physically induced stress fatigue and radiation-induced tensile stresses in the surface layers

of the resin as a result of shrinkage during weathering. Unlike fibre prominence, which occurs on either side of the sheet, microcracking is confined to the surface layers (5 to 10 μm) of the exposed surface.

Fire-retardant GRP sheets have considerably lower resistance to breakdown when exposed to the outdoor environment. Tests have shown that one common type of fire-retardant GRP sheet (based on tetrachlorophthalic acid polyester) undergoes surface deterioration 2.5 to 3 times faster than sheets based on general purpose (conventional) polyester matrix.

As most of the deterioration is confined to the surface material, the surface region can be modified to increase the resistance of the GRP sheet to breakdown. For example, a gelation coat as a surface finish of GRP sheets protects the glass-resin interface against the effect of moisture and temperature-induced stress-fatigue so that no fibre prominence occurs. Good resistance to both types of deterioration is achieved by coating the GRP sheets with a lacquer based on ultraviolet (uv) light stabilized acrylic resin. The acrylic coating protects the glass-resin interface against the effect of stress-fatigue and the underlying matrix against the action of ultraviolet light.

Although the appearance of GRP sheets weathered outdoors for five years was considerably affected, deterioration in mechanical properties such as tensile strength was generally moderate; for example, the exposed sheets retained 85 to 92 percent of their initial (before exposure) tensile strength. If the surface breakdown is in an advanced stage, it can, however, have a serious effect on the mechanical properties of the GRP composite and on the light transmission of transparent or translucent panels.

Because the matrix is a plastic material and thus organic in nature and inherently combustible, GRP composites will decompose and burn when exposed to a fire. The architect or design engineer using GRP materials should, therefore, have a full understanding of their potential fire hazard and fire behaviour (Blaga, 1978).

1.2.6 Problems in Recycling Thermoset Composites

Pickering (2005) stated that the problems in recycling thermoset composites are given as; thermosetting polymers are cross linked and cannot be remoulded, in contrast to thermoplastics which can easily be remelted. Some thermosetting polymers can be converted relatively easily back to their original monomer, such as polyurethane. It is well known that, thermosetting resins, such as polyester and epoxy are not practical to depolymerise to their original constituents.

Composites are by their very nature mixtures of different materials: polymer, fibrous reinforcement (glass or carbon fibre) and in many cases fillers (these may be cheap mineral powders to extend the resin or have some other function, such as fire retardants). There are few standard formulations and for most applications the type and proportion of resin, reinforcement and filler are tailored to the particular end use.

Composites are often manufactured in combination with other materials. For example, there may be foam cores to reduce weight and cost or metal inserts to facilitate fastening onto other components. In addition to these specific problems, there are the other problems associated with recycling any material from end-of-life components, such as the need be able to deal with contamination and the difficulty of collecting, identifying, sorting and separating the scrap material.

European legislation now requires that recycling routes are available for composites, as other waste management methods will not be allowed. The European composites industry is responding with a ECRC to manage waste from composites and stimulate recycling activities. Recent changes to waste management legislation and likely future directions mean that recycling routes are urgently needed to be in place for thermoset composite materials if they are to continue to have a place in the market. Recognising that composite recycling activities need stimulation and financial assistance if they are to succeed, the European Composites Industry Association (formerly the GPRMC) is proposing a ECRC.

1.3 Technologies of Recycling of Glass Fiber Reinforced Polyester

1.3.1 Incineration of GRP Waste

According to Siddique et al., 2008, the heat content of plastic wastes can be recovered by incineration. Plastic wastes are a good fuel source because most resins have a heating value almost equivalent to that of the coal. In addition to providing an attractive source of alternative energy, preserving natural resources and minimizing the impact of dependency on energy, incineration also greatly reduces the volume of garbage by about 90–95%. But, there is always public resistance emerging against incineration because of the emission of some toxic fumes. However, current technology makes it possible to operate incineration plants in a way that emissions would not be a problem and, therefore, would conform to the Clean Air Act Amendments of 1990 (Alter, 1993 and Yakowitz, 1990).

Two types of ash are produced by an incineration process; fly ash (the very fine particles entrained in incinerator exhaust gases) and bottom ash (the large and heavy particles removed from the bed of the incinerator), which require disposal. Landfilling these ash residues may not always be acceptable because of the potential for groundwater and soil pollution due to leachate carrying heavy metals such as lead and cadmium. Methods of protecting groundwater and soil from leachate, such as lining the landfill, can be expensive and are not always effective from an environmental standpoint. Accordingly, some research is being undertaken to effectively stabilize and recycle incineration residues in construction applications (Goumans et al., 1991).

1.3.2 Using Subcritical Fluids and Separating the Components of the Unsaturated Polyester

Tomoko et al., 2008 developed a new recycling method using subcritical fluids where unsaturated polyester resin in GRP can be efficiently depolymerized to separate glass fiber from filler and polymer. Reactions were carried out with or without a activator (K_3PO_4) in diethyleneglycol monomethylethter (DGMM) and

benzyl alcohol(BZA) under their subcritical state at temperatures 463–623 K for 1–8 h in a batch reactor. The conversion of UP became fast as the activator/solvent molar ratio increased and it was enhanced in the presence of K_3PO_4 activator in subcritical BZA. The glass fiber recovered after the FRP treatment in subcritical BZA was relatively long, while it became short and somewhat damaged at temperature higher than 573 K. The similar trend was observed when DGMM was used as a solvent.

1.3.3 Pyrolysis and Thermal Gravimetric Behaviour of GRP Composites

According to Cunliffe et al, 2003 used a static-bed bench-scale reactor, as shown in Figure 1.4., to pyrolyse the composite samples. Nitrogen was passed through the reactor during the experiments to sweep the derived pyrolysis gases out of the hot zone of the reactor and thereby prevent secondary reactions of the pyrolysis vapours and also to aid in the quantification of the product gases. The sample was heated at $10\text{ }^{\circ}\text{C}/\text{min}$ to final temperatures between 350 and 800°C , held at the final pyrolysis temperature for 60 min, then allowed to cool under nitrogen. The average product recovery from all the experiments represented over 98% of the initial sample mass.

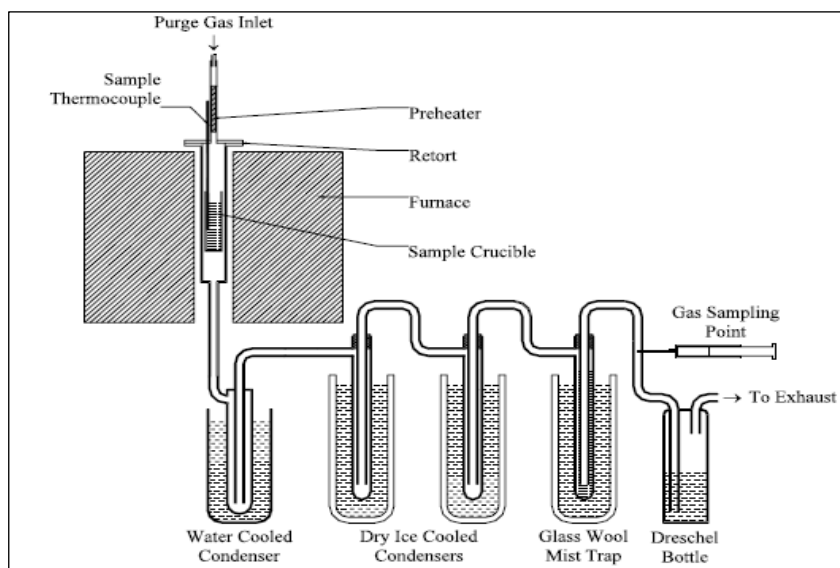


Figure 1.4 A diagram of the bench-scale pyrolysis reactor (Cunliffe et al, 2003).

Cunliffe and Williams, (2003), pyrolysed glass fibre reinforced polyester plastic waste in a fixed-bed reactor at 450 °C (Figure 1.5). The glass fiber present in the solid residue recovered after pyrolysis could be easily separated from the residue via oxidation of the carbon and sieving of the resultant filler and fiber mixture. The glass fibre recovered from the solid residue had mechanical properties which indicated that they could replace up to 20 wt% of virgin glass fibre in Dough Moulding Compound(DMC). The glass fibres have successfully been re-used in test plaques and sample pieces as DMC in polyester composites.

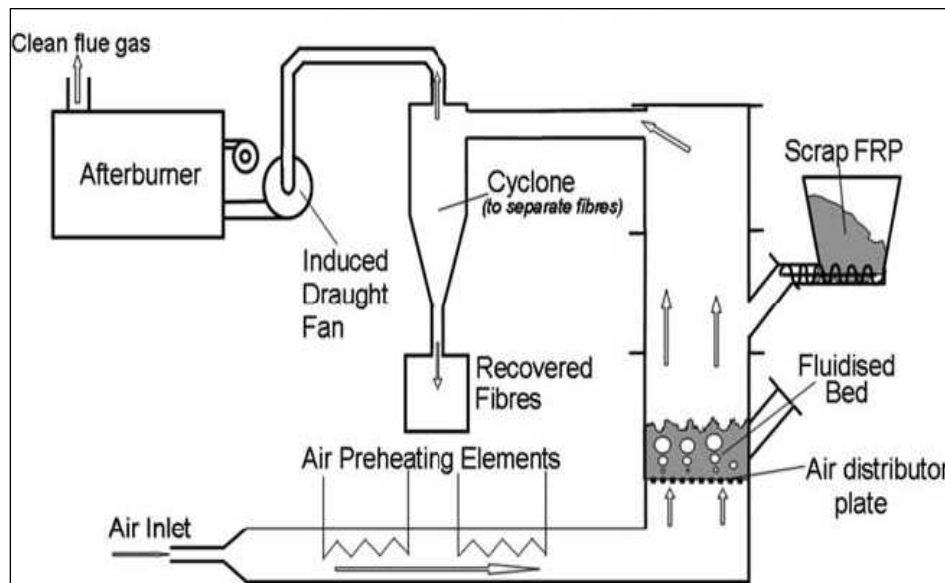


Figure 1.5 A schematic diagram of a fluidised bed thermal process (Pickering, 2006)

Cunliffe et al, 2003, used TGA instrument to study the pyrolysis of the composite samples. The sample was heated at 10 °C/ min to 900 °C, with nitrogen passing through the furnace at 50 ml/min. The furnace temperature was then increased by 10 °C to trigger the gas supply to change over to air, and held at this temperature for 15 min. The sample weight was recorded against time and temperature at 4 s intervals to produce a thermogram (TG). Figure 1.6 clarifies the nomenclature adopted in the discussion of the dTG plots.

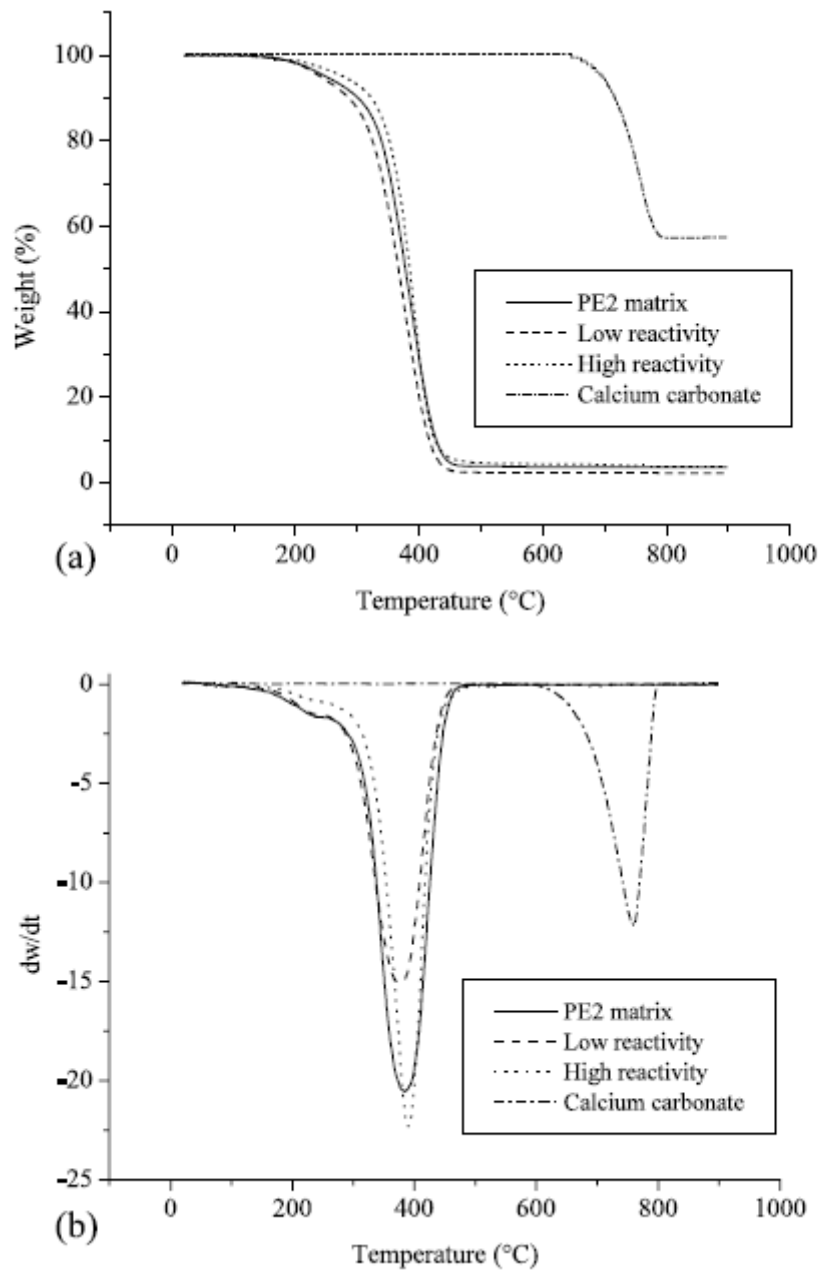
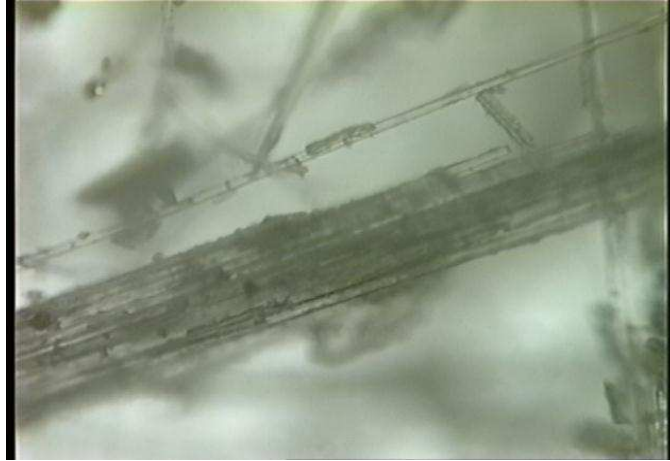
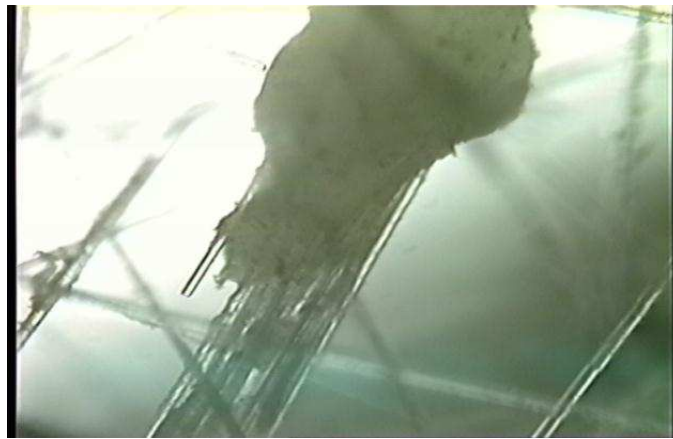


Figure 1.6 Plots derived from the TGA pyrolysis of three pure polyester resins and calcium carbonate (a)TG curves (b)dTG curves, Cunliffe et al, (2003).

Optical image of the loose fibers that make up one portion of recyclate. (Figure 1.7). Clearly the fibers have both resin and filler bonded to them. The other particles making up the recyclate are larger particles of resin, filler, and fiber. Unlike the loose fibers, the particles included of a significant portion of resin and filler.



(a)



(b)

Figure 1.7. Optical microphotographs (a) Optical image of the loose fibers that make up one portion of recyclate. (b) The other particles making up the recyclate are larger particles of resin, filler, and fiber.

1.3.4 Recycling by Regrinding

GRP were used by the auto industry alone making it one of the highest volume composites and therefore most in need of recycling.

The regrinding recycling process involves the incorporation of finely powdered polymer matrix back into the same application. This technology is best suited for the low levels of production scrap or for low-volume post customer waste (Scheirs, 1998).

The primary recycling of a plastic manufacturing scrap by regrind recycling offers the best return for the recycle investment since it allows the manufacturer to reduce raw material costs at the production stage with a modest capital expenditure. This is the case with GRP regrind when it is used as an extender (non-reinforcing filler) back into similar applications. This process involves size reduction of the scrap by two operations: first granulation followed by fine grinding (Scheirs, 1998).

Material recycling, in which the recovered scrap is incorporated into new generation of composite materials. Generally, filler material Calcium Carbonate (Calcite), talc, dolomite can be used as filler most commonly.

Kouparitsas, 2002 obtained the composite scrap, and then incorporate it into a new composite structure. In most cases this grinding approach includes the initial cutting of the thermoset composite into smaller pieces and then grinding these pieces to produce a very fine powder, which is reused as an active filler, thus replacing standard commercial fillers. Typical equipment for the grinding of thermoset composites includes: a) a basic granulator or a hammer mill, b) a pulverizer for turning the ground material in powder form and c) a classifier for separating the different fractions.

In the case of fiber reinforced composites, and depending on the type of the granulator used as well as the extent of grinding, the recovered material may be classified in two distinct categories: a) a fibrous fraction containing the largest portion of the reinforcement agents (fibers), b) a fine powder fraction containing the bigger part of the polymeric matrix. This fragmentation is important for an optimum recycling, without any further treatment. In particular, fibrous fraction reuse seems promising as reinforcement in Bulk Molding Compound (BMC) composites. On the other hand, resin-rich fine fractions are useful reinforcements in either BMC or Sheet Molding Compound (SMC) composites. Then, and in order to avoid producing recycled composites with unpredictable properties, it is important not to mix different polymeric matrixes or reinforcements (Kouparitsas, 2002).

2. EXPERIMENTAL STUDY

2.1 Materials

2.1.1 Matrix

Orthophtalic unsaturated polyester which its commercially name is CE 92 N8, obtained from Poliya Poliester Ltd .

2.1.2 Fillers

Nonwoven glass fibers (425gr/m^2), produced by Cam Elyaf A.Ş. Calcite was obtained from OMYA.

GRP dust were the wastes of Fibrosan.



Figure 2.1. The waste GRP during production of GRP coating sheets (photo courtesy of E.Yucel, Fibrosan Inc.)



Figure 2.2. Waste GRP after production (photo courtesy of E.Yucel, Fibrosan Inc., Izmir, Turkiye)

Table 2.1 Properties of reinforcing glass fiber (Chawla K.K., 1998)

| Characteristic | Glass Fiber |
|--|--------------------|
| Diameter (μm) | 8 - 14 |
| Density (g/cm^3) | 2,55 |
| Young's modulus(GPa) parallel to fiber axis | 70 |
| Young's modulus(GPa) perpendicular to fiber axis | 70 |
| Tensile Strength (GPa) | 1,5 - 2,5 |
| Strain to fracture (%) | 1,8-3,2 |
| Coefficient of thermal expansion(10^{-6} K^{-1}) parallel to fiber axis | 4,7 |
| Coefficient of thermal expansion(10^{-6} K^{-1}) perpendicular to fiber axis | 4,7 |

2.1.3 Additives

Two type wastes, dust and production wastes which are shown Figure 2.1 and Figure 2.2. The photos of waste GRP obtained during production by courtesy of E. Yucel, Fibrosan Inc.

Initiator(methyl ethyl ketone peroxide, 40% in dimethyl phtalate), Akzo-Nobel and activator (Cobalt naphtanate, 1%) are used in curing reactions of composites.

2.2 Method

2.2.1 Grinding and Sieve Analysis

Grinding of GRP waste were done by using Fimak grinding machine and the sizes of sieves were 2.0, 1.0, 0.5 mm. and fine sieve method of waste of production dust of cutted edge of sheets in Fibrosan Inc.

In the second part of the experiment gelation, tensile and flexural properties of composite sheet samples were determined.

Six composite samples were prepared. The weight percentages of GRP dust or calcite were 0%, 5%, 15%, 20%, 25%, 30% based on polyester used.

Table 2.2 Experimental weight percents of ingredients of composite samples

| <i>Ingredient</i> | <i>w,Filler/w,Bulk</i> | | | | | |
|--------------------------------|------------------------|-----------|------------|------------|------------|------------|
| | <i>%0</i> | <i>%5</i> | <i>%15</i> | <i>%20</i> | <i>%25</i> | <i>%30</i> |
| w,Filler/w,Composite% | 0 | 4 | 13 | 17 | 21 | 26 |
| w,Virgin GRP/ w,Composite % | 15 | 15 | 15 | 15 | 15 | 15 |
| w,UP/w,Composite % | 85 | 81 | 72 | 68 | 64 | 59 |



(a)



(b)

Figure 2.3 (a) Grinding Machine, made by Fimak Co. (b) The grinded GRP waste after grinding process (photo courtesy of E.Yucel, Fibrosan Inc.)



a

b

c

Figure 2.4 Different sizes of waste GRP a) greater than 2 mm b) between 2 mm to 0.5 mm c) less than 0.5mm

There were sieves with different sizes, 2.0, 1.0 and 0.5 mm. The Figure 2.4 shows that different sizes of ground waste after fine sieve process.

Sieve analysis of waste GRP dust obtained directly from the cutting edge of sheets were made by different sizes as 500, 315, 250 and 125 μm .

2.2.2 GRP Composite preparation method

The experimental set-up was used in the laboratory of Fibrosan Inc. GRP consists of three elements, that were, nonwoven type glass fiber, unsaturated orthophthalic polyester (UP) resin, filler and calcite.

Hand lay up technique was the simplest composite processing technique. Fibers can be laid into a mold by hand and the resin UP was brushed with hand roller. Frequently, resin and fibers are brushed together into the mold surface. Curing may be done at room temperature or at a moderately high temperature in an oven (Chawla, 1998).

GFR composite was made from hand layup process with bulk and nonwoven glass fiber. Transparent film layer was used for protect the experimental GRP sheets. All experiments were accomplished at 23°C climatized room.

2.2.3 Analysis of Gelation Behaviour

Determination of gelation properties mainly accomplished by measuring the temperature of the mixed polyester plus GRP dust and/or calcite. The percentage of filler were 0%, 5%, 15%, 20%, 25%, 30% based on UP resin and filler, initiator (MEK peroxide, 1%) and activator (Cobalt naphthanate, 1%). Gelation time was observed with a chronometer by stirring the system with a glass stick, the gelation time was observed as the solidification of the liquid mixture by naked eye.

Testo exotherm device; 1775 - T3 was used for determination the peak time, peak temperature as exotherm parameters.



Figure 2.5 Experimental set up for hand lay up proces in Fibrosan laboratory, Izmir

2.2.4 Tensile Measurements

The AGS-J Shimadzu Autograph Flexural test machine was used for tensile strength and tensile modulus measurements.

ISO 527- 4 was International Standard that explains the determination of tensile properties of plastics for test conditions for isotropic and orthotropic fiber reinforced plastic composites.

2.2.5 Flexural Measurements

The AGS-J Shimadzu Autograph Flexural test machine was working by center loaded type, 10 kN and 150 mm gauge length. The photograph of AGS-J Shimadzu Autograph Flexural test machine was shown in Figure 2.6.



Figure 2.6 The AGS-J Shimadzu Autograph Flexural test machine

Prepared composite sheet samples having thicknesses between 1.6-2.0 mm were cutted into 25mm width by cutting aparatus. A photograph of experimental GRP composite sheet samples after hand layup process were shown in Figure 2.7.

ISO 14125 was International Standard that explains the determination of flexural properties for fiber reinforced plastic composites.



Figure 2.7 The experimental GRP composite sheet samples after hand layup process

3. RESULTS AND DISCUSSION

3.1 Grinding and Sieve Analysis

It was understood that ground GRP waste can be reused in new composite formulations. The critical factor in the reuse of GRP dust was the particle size and its distribution. Table 3.1 shows fractions which were obtained from GRP scrap composite after grinding process.

Table 3.1 Fractions obtained from GRP scrap composite after grinding process

| Screen size,mm | Reground fraction | w/w % |
|----------------|--------------------------|-------|
| + 2,0 | Separated short GRP | 57 % |
| + 1,0 | Very short GRP | 21 % |
| + 0,5 | Coarse UP pieces and GRP | 14 % |
| - 0,5 | Fine GRPdust | 8 % |

As it was seen in Table 3.1; 43% of GRP is ground below 2.0mm, it could be understood that complete grinding should need a specially designed grinding machine.

The GRP dust used in recycling experiments has the sieve analysis in Table 3.2. It was directly obtained from the process and no other classification was applied.

Table 3.2 Sieve analysis of waste GRP dust obtain directly from the cutting of edge of sheets

| Screen Size, μm | Reground fraction | w/w % |
|----------------------------|-------------------|-------|
| + 500 | Fine GRP dust | 1 % |
| + 315 | Powder | 30 % |
| + 250 | Powder | 27 % |
| + 125 | Powder | 28 % |
| - 125 | Powder | 14 % |

3.2 Analysis of Gelation Behaviour

The results were seen in Table 3.3.

Table 3.3 The results of exotherm parameters obtained from Testo logger device.

| % w/w Filler in Bulk | Filler Type | Gelation Time (Sec) | Peak Time, (Sec) | Peak Temp, $^{\circ}\text{C}$ |
|----------------------|-------------|---------------------|------------------|-------------------------------|
| 0% | Pure resin | 485 | 1500 | 174 |
| 5% | Calcite | 455 | 1260 | 181 |
| | Dust | 398 | 1200 | 180 |
| 15% | Calcite | 368 | 1080 | 175 |
| | Dust | 396 | 1200 | 170 |
| 20% | Calcite | 365 | 1260 | 163 |
| | Dust | 392 | 1260 | 162 |
| 25% | Calcite | 361 | 1260 | 147 |
| | Dust | 385 | 1260 | 148 |
| 30% | Calcite | 352 | 1260 | 156 |
| | Dust | 362 | 1140 | 155 |

It was well-known that calcite was a good filler for composite materials. Peak temperature was nearly same after addition of GRP dust as filler instead of calcite. The change of curing temperature is seen in Figure 3.1.

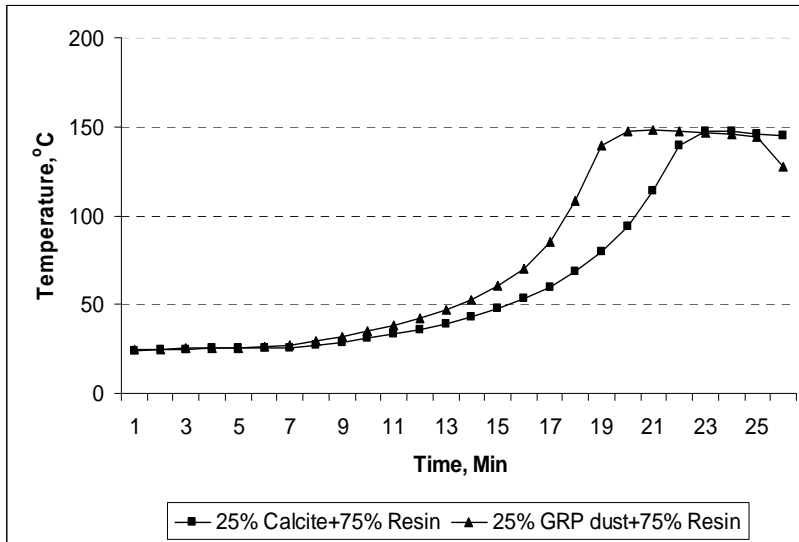


Figure 3.1 Exotherm graph for 25% weight of filler with curing time (Other results of exotherm graphs in Appendix I, about 5%, 15%, 20%, 30%).

Histogram graphics for comparison of peak temperatures of filled composites were shown in Figure 3.2.

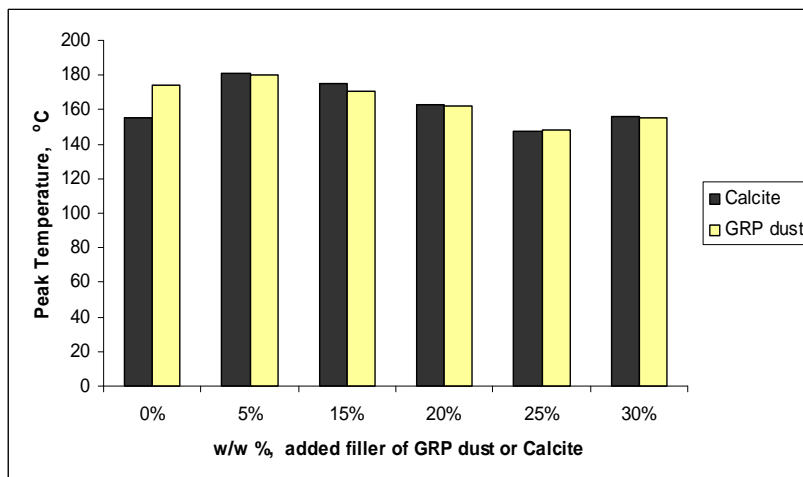


Figure 3.2 Histogram for comparison of peak temperatures of added fillers.

Gelation time decreases by the filler addition but the decrease is slightly higher in the case of GRP dust. It seems GRP dust acts as a curing catalyst in these systems due to the residual unsaturation which becomes active and forms additional radical sites.

3.2 Flexural Analysis

On the other hand, flexural testing indicates that virgin material performs well, and compare favorably with a reference set of samples containing GRP dust recycle.

Table 3.4 Flexural strength for the composite samples with calcite and GRP dust.

| % , weight | Calcite, MPa | GRP dust, MPa |
|-------------------|---------------------|----------------------|
| 0 | 195 | 195 |
| 5 | 106 | 133 |
| 15 | 155 | 142 |
| 20 | 140 | 138 |
| 25 | 110 | 84 |
| 30 | 130 | 87 |

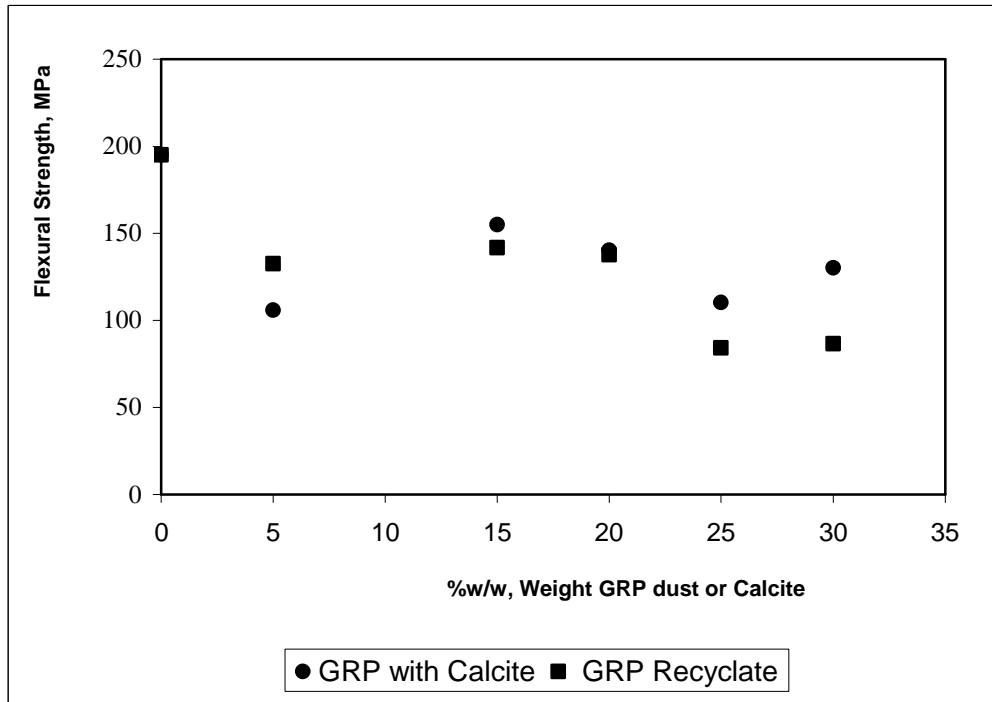


Figure 3.3 Flexural strength of composite with calcite and GRP dust recyclate.

The Figure 3.3 shows that calcite or GRP dust causes to decrease the flexural strengths of composites..

Table 3.5 Flexural modulus for the composite samples with calcite and GRP dust.

| % , weight | Calcite, MPa | GRP dust, MPa |
|------------|--------------|---------------|
| 0 | 8310 | 8310 |
| 5 | 7812 | 6250 |
| 15 | 7583 | 8356 |
| 20 | 6009 | 7995 |
| 25 | 5427 | 6044 |
| 30 | 4849 | 6477 |

The Figure 3.4 shows that flexural modulus of composite with calcite and GRP dust recycle decreases with the increase of percentage weight of added fillers. The decrease of modulus is seen as a nonlinear way, up to 20% of calcite addition a slight decrease and then a rapid decrease could be seen. In the case of GRP dust , a continuous decrease is seen.

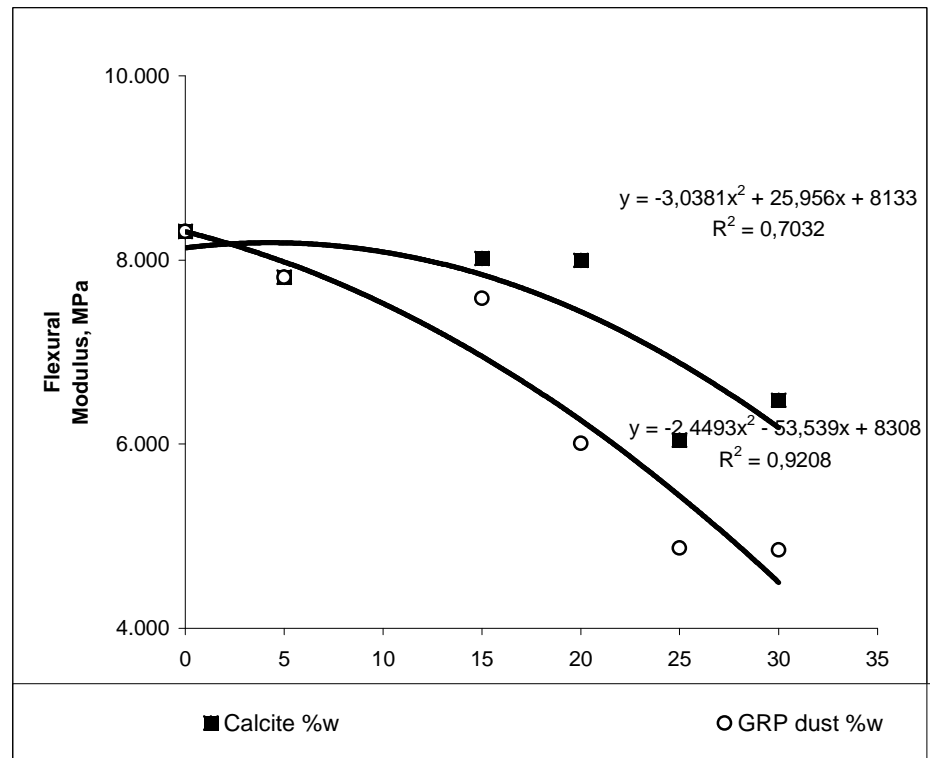


Figure 3.4 Flexural modulus of composite with calcite and GRP dust recycle.

3.3 Tensile Analysis

Data obtained for calcite and GRP dust and calcite for tensile strength for the sheet samples are given in Table 3.6.

Table 3.6 Tensile tests of calcite added as filler in bulk.

| % , weight | Tensile Strength, MPa | Tensile Strain, % | Tensile Modulus MPa |
|-------------------|------------------------------|--------------------------|----------------------------|
| 0 | 82.3 | 2.5 | 5774.4 |
| 5 | 64.5 | 2.3 | 3873.4 |
| 15 | 61,6 | 2.3 | 3684.1 |
| 20 | 54.4 | 1.8 | 3639.2 |
| 25 | 54.3 | 1.6 | 4229.4 |
| 30 | 55.2 | 1.8 | 4294.5 |

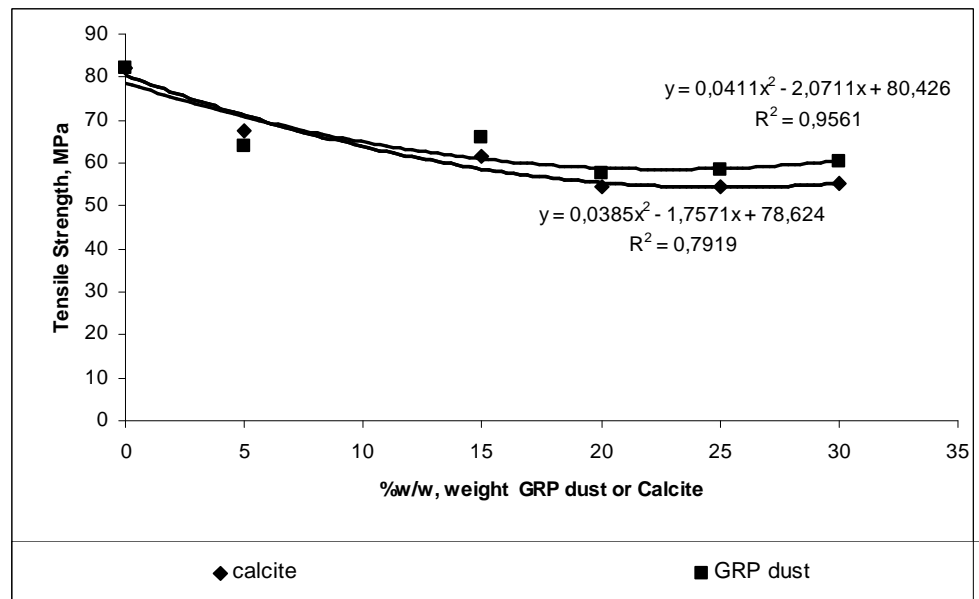
Table 3.7 Tensile tests of GRP dust added as filler in bulk.

| Weight % | Tensile Strength MPa | Tensile Strain % | Tensile Modulus MPa |
|-----------------|-----------------------------|-------------------------|----------------------------|
| 0 | 82.3 | 2.52 | 5774.4 |
| 5 | 63.9 | 2.46 | 4116.0 |
| 15 | 65.9 | 2.33 | 3990.5 |
| 20 | 57.8 | 2.00 | 3863.3 |
| 25 | 58.4 | 1.99 | 3489.1 |
| 30 | 60.2 | 2.20 | 3904.3 |

Figure 3.5 shows the variations of tensile strength of composite sheet sample with calcite and GRP dust recycle. As it is expected, tensile strength of sheets with calcite and GRP dust decreases by increasing weight percentage of filler.

Table 3.8 Tensile strength for the composite samples with calcite and GRP dust.

| % , weight | Calcite, MPa | GRP dust, MPa |
|------------|--------------|---------------|
| 0 | 82.3 | 82.3 |
| 5 | 64.5 | 63.9 |
| 15 | 61.6 | 65.9 |
| 20 | 54.4 | 57.8 |
| 25 | 54.3 | 58.4 |
| 30 | 55.2 | 60.2 |

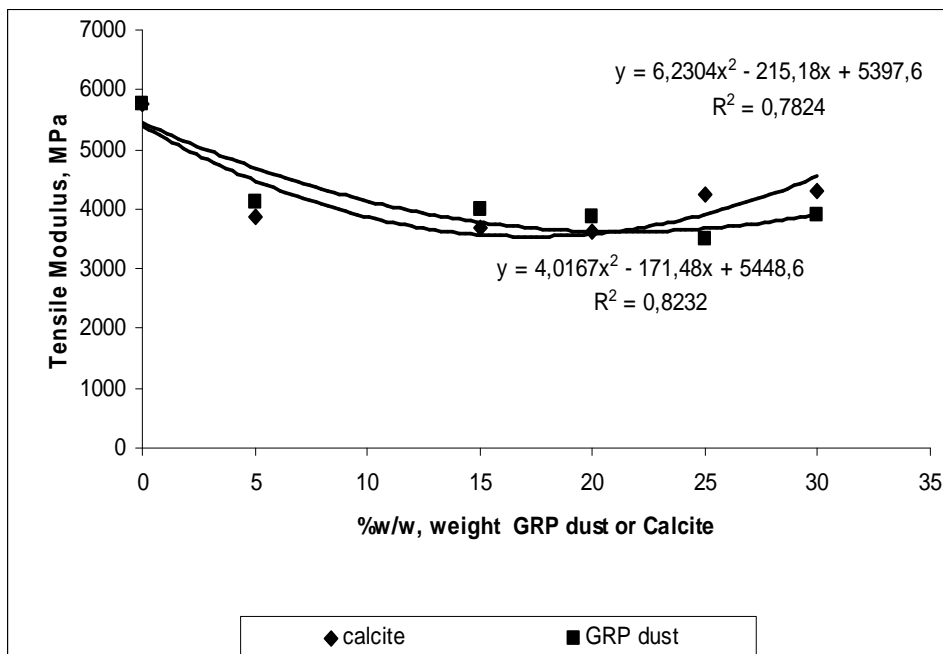
**Figure 3.5** Tensile strength of composite with calcite and GRP dust recycle.

Tensile modulus is also important parameter for composite systems the values for both calcite and GRP dust added samples are given in Table 3.9.

Table 3.9 Tensile modulus for the sheet sample.

| % weight | Calcite, MPa | GRP dust, MPa |
|----------|--------------|---------------|
| 0% | 5774,4 | 5774,4 |
| 5% | 3873,4 | 4116 |
| 15% | 3684,1 | 3990,5 |
| 20% | 3639,2 | 3863,3 |
| 25% | 4229,4 | 3489,1 |
| 30% | 4294,5 | 3904,3 |

As seen in Figure 3.9, tensile modulus of composite sheet samples with calcite and GRP dust recycle decrease by increasing weight percentage adding filler.

**Figure 3.6** Tensile modulus composite with calcite and GRP dust recycle

In flexural and tensile test experiments, hand lay up technique was used and slight deviations inevitably occur in thicknesses of specimens so the result was scattering of the data obtained from mechanical tests.

4. CONCLUSION

In this study, GRP waste was considered as a filler, curing and mechanical properties were compared with the properties of calcite added samples. Similar results were obtained in both calcite and GRP dust added samples. In fact some reinforcement of GRP dust added composite was expected due to the fibrous structure of the waste but short fibrous structure of GRP and weak interfacial bonding strength of the mixture due to the absence of coupling agents led to low strength composite materials. If the breakage of fibre length during grinding could have been controlled by using a specially designed grinding machine, the mechanical properties might have been expected to be higher than the calcite added materials.

Gelation time with GRP dust is slightly lower than the time of calcite, the difference of peak temperatures of these two fillers is very low and the time needed for the systems to reach to this temperature is also low which is nearly two minutes .

If we consider to reuse these wastes as 5% w/w addition to virgin composite mixture, tensile strength will fall by 22%, and modulus by 30%. In certain applications this decrease might be tolerated very well. Similar results could also be obtained from flexural data.

In conclusion, we can easily recognise the problem of landfilling and apart from the economics of the process of the addition of GRP dust, we need to reuse these wastes as a filler and as a replacement of calcite.

REFERENCES

- Alter, H.**, 1993, The origins of municipal solid waste: II. Policy options for plasticswaste management, *Waste Management Research*, 11, 319– 332pp.
- Bıçakoğlu B.**, 2007, Cam Elyaf Focuses on Further Growth, *Reinforced Plastics*, 34-37pp.
- Blaga, A.**, 1979, GRP Composite Materials in Construction: Properties, Applications and Durability. *Industrialization Forum*, (9): 27-32pp.
- Brandrup J., Bittner M., Menges G., Michaeli W.**, 1996, Recycling and Recovery of Plastics, Hanser Publishers Inc., Cincinnati, 893p.
- Brydson J.A.**, 1989, Plastic Materials, Butterworth Heinemann, London, 839p.
- Cam Elyaf Sanayii A.Ş. Elyafli Malzemeler Grubu**, 1984, CTP Teknolojisi-Camelyafi Takviyeli Reçine Sistemleri, İstanbul, 199s.
- Cavalieri, F., Padella, F.**, 2002, Development of composite materials by mechanochemical treatment of post-consumer plastic waste, *Waste Management* 22 (8): 913–916pp.
- Chawla K.K.**, 1998, Composite Materials, Birmingham, Springer, 483p.
- Crawford R.J.**, 1987, Plastic Engineering, Pergamon Press, the Queen's University of Belfast, UK, 354p.
- Cunliffe A. M. and Williams P.T.**, 2003, Characterisation of products from the recycling of glass fibre reinforced polyester waste by pyrolysis, MSc Thesis , The University of Leeds, Leeds LS2 9JT, UK.
- Cunliffe A.M., Jones N., Williams P.T.**, 2003, Pyrolysis of composite plastic waste, *Environ Technol*, (24):653–663pp.

REFERENCES(continued)

- Curlee, T.R.**, 1986, *The Economic Feasibility of Recycling: A Case Study of Plastic Wastes*. Praeger, New York.
- Eldin, N.N., Senouci, A.B.**, 1992, Use of scrap tires in road construction, *Construction Engineering Management*, ASCE 118 (3): 561– 576pp.
- Ernst, T., Popp, R., Eldik, R.V.**, 2000, Quantification of heavy metals for the recycling of waste plastic from electrotechnical applications, *Talanta* 53 (2): 347–357pp.
- Goumans, J., Van der Sloot, H., Albers, T.**, 1991, Waste materials in Construction, *Studies in Environmental Science*, Elsevier Science Publishing Company Inc., New York, vol. 48.
- Hall, W.J., Williams, P.T.**, 2007. Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment. *Journal of Analytical and Applied Pyrolysis* 79 (1–2), 375–386pp.
- Hayashi, F., Oshima, M., Koyanagi, W.**, 1996. Thermal properties and temperature dependence of mechanical properties of resin concretes for structural use, *Structural Materials* 45 (9): 1014–1020pp.
- Hollaway L.**, 1978, *Glass Reinforced Plastics in Construction*. Engineering Aspects. New York, Wiley,.
- Kouparitsas C.E., Kartalis C.N., Varelidis P.C., Tsenoglou , Papaspyrides C.D.**, 2002, Recycling of the Fibrous Fraction of Reinforced Thermoset Composites, *Polymer Composites*, 23(4): 682-688pp.
- Larsen K.**, 2009, Recycling wind, *Reinforced Plastics*, 53(1): 20- 23pp.

REFERENCES (continued)

- Masuda, T., Kushino, T., Matsuda, T., Mukai, S.R., Hashimoto, K., Yoshida, Shu-ichi**, 2001, Chemical recycling of mixture of waste plastics using a new reactor system with stirred heat medium particles in steam atmosphere, *Chemical Engineering Journal*, 82 (1–3): 173–181pp.
- McQuillen, J.L., Takallou, H.B., Hicks, R.G., Esch, D.**, 1998. Economic analysis of rubber modified asphalt mixes, *Journal of Transportation Engineering*, ASCE 114 (3): 259–277pp.
- Miskolczi, N., Bartha, L., Dea'k, G., Jo' ver, B.**, 2004. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons, *Polymer Degradation and Stability* 86 (2): 357–366pp.
- Osswald T. A.**, 1998, polymer processing Fundamentals, Hanser Publisher, Inc., 220p.
- Pickering S. J.**, 2006, Recycling Technologies for Thermoset Composite Materials Current Status, *Composites A* 37, (8): 1206-1215pp.
- Pickering S. J., Benson M.**, 1991, The recycling of thermosetting plastics, Plastics and rubber institute, Second international conference plastics recycling; London, 23/1–10pp.
- Pickering S.J., Kelly R.M., Kennerley J.R., Rudd C.D. and Fenwick N.J.**, 2000, A fluidised bed process for the recovery of glass fibres from scrap thermoset composites, *Compos Sci Technol*, (60): 509–523pp.
- Pickering S. J., Benson M.**, 1993, Recovery of materials and energy from thermosetting plastics Sixth European composite materials conferenced, recycling concepts and procedures. Bordeaux, France, *European Association for Composite Materials*; 41–46pp.

REFERENCES (continued)

- Remias J.E., Pavlosky T.A., Sen A.,** 2000, Oxidative chemical recycling of polyethene. *Comptes Rendus de l'Académie des Sciences – Series IIC – Chemistry* 3 (7): 627–629pp.
- Scheirs J.,** 1998, *Polymer Recycling - Science Technology and Applications*, Wiley, London, 591p.
- Schutte L. C.,** 1994, Environmental durability of glass fiber composites, Polymer Composites Group, Polymers Division, *National Institute of Standards and Technology*, Gaithersburg, MD 20899, USA,
- Siddique R., Khatib J , Kaur I.,** 2008, Use of recycled plastic in concrete, *Waste Management* (28): 1835–1852pp.
- Siddique R., Naik T.R.,** 2004. Properties of concrete containing scrap tire rubber – an overview. *Journal of Waste Management* 24 (6), 563– 569pp.
- Skrifvars M.,** 2003, Introduction to composites recycling. COMPOSIT thematic network workshop, Recycling of composite materials in transport, SICOMP, Pitea, Sweden; Papers available at: <http://www.compositn.net>.
- Soroushian P., Plasencia J., Ravanbakhsh S.,** 2003. Assessment of reinforcing effects of recycled plastic and paper in concrete. *ACI Materials Journal* 100 (3): 203–207pp.
- Stein, R.S.,** 1992, Miscibility in polymer recycling-emerging technologies in plastics recycling, ACS Symposium Series 513, *American Chemical Society*, 39–48pp.
- Subramanian, P.M.,** 2000, Plastics recycling and waste management in the US. Resource, *Conservation and Recycling* (28): 253–263pp.
- Telfeyan E.,** Recycling of Glass Fiber Composite, Derosaposter, NYS College of Ceramics· Alfred University, 1p.

REFERENCES (continued)

- Thomas W. F.**, 1960, An investigation into the factors likely to affect the strength and properties of glass fibres, *Phys Chem Glasses*; 1(1): 4–18pp.
- Tomoko I., Shinpei T., Mitsuru S., Motonobu G., Katsuji S.**, 2008, Recycling of fiber reinforced plastics using depolymerization by solvothermal reaction with activator , *J Mater Sci*, (43) : 2452–2456pp.
- Torres A., de Marco I., Caballero B.M., Laresgoiti M.F., Legarreta J.A., Cabrero M.A.**, 2000, Recycling by pyrolysis of thermoset composites: characteristics of the liquid and gaseous fuels obtained, *Fuel*, (79): 897–902pp.
- Williams P.T.**, Recycling aerospace composites for recovery of high value carbonfibres and resinchemicals, the University of Leeds, LS2 9JT, UK, 21p.
- Yakowitz, H.**, 1990, Incineration of municipal solid waste: scientific and technical evaluation of the state-of-the art by an expert panel, *Resources, Conservation and Recycling*, (4): 241–252pp.

APPENDIX

APPENDIX I : Exotherm graphs of each composites sheet samples

APPENDIX I

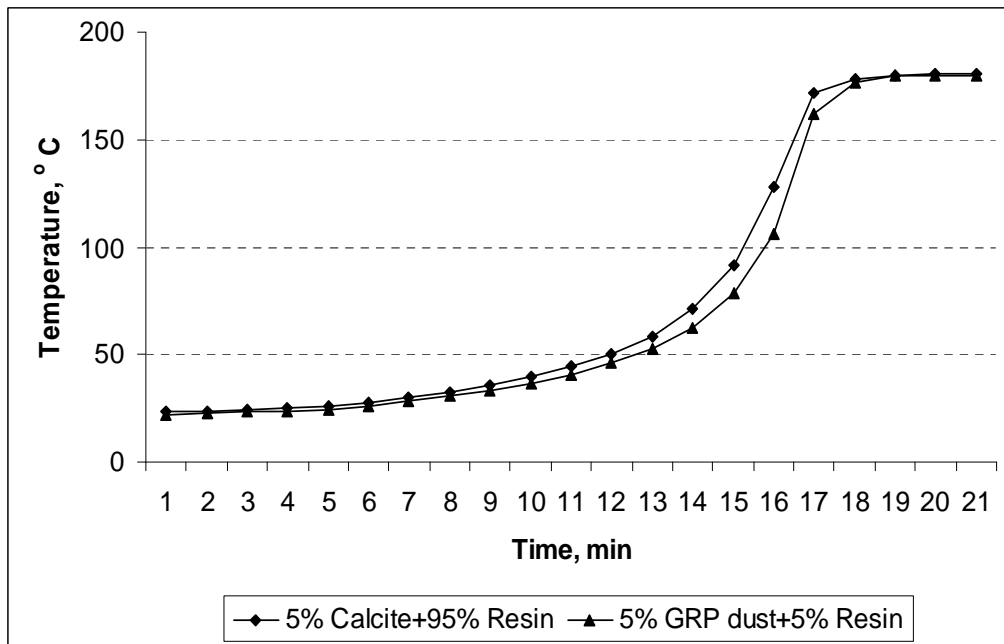


Figure I.1 Exotherm graph for 5% weight of added fillers with curing time

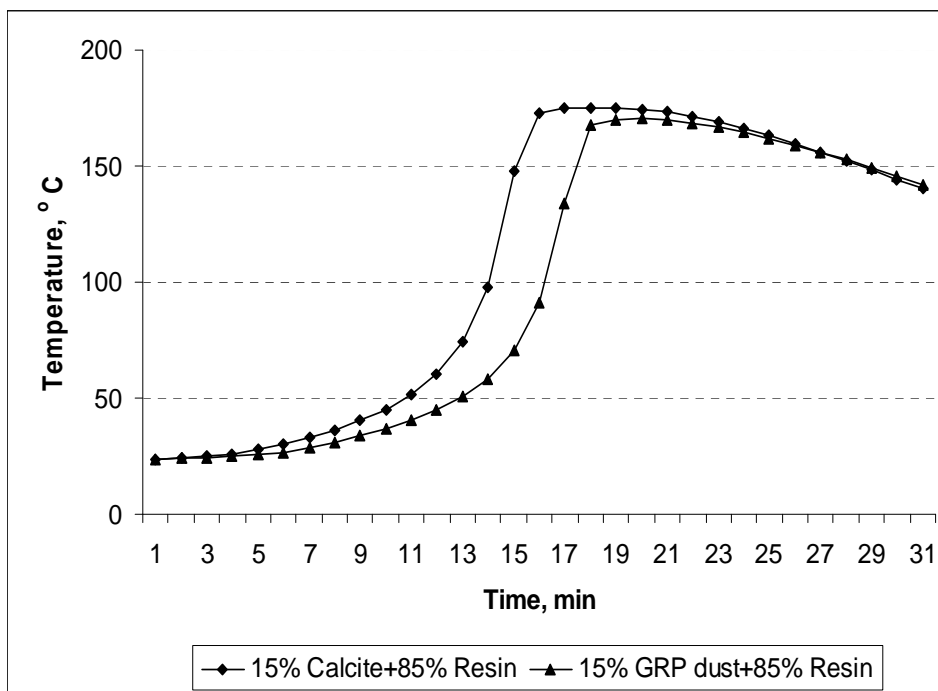


Figure I.2 Exotherm graph for 15% weight of added fillers with curing time

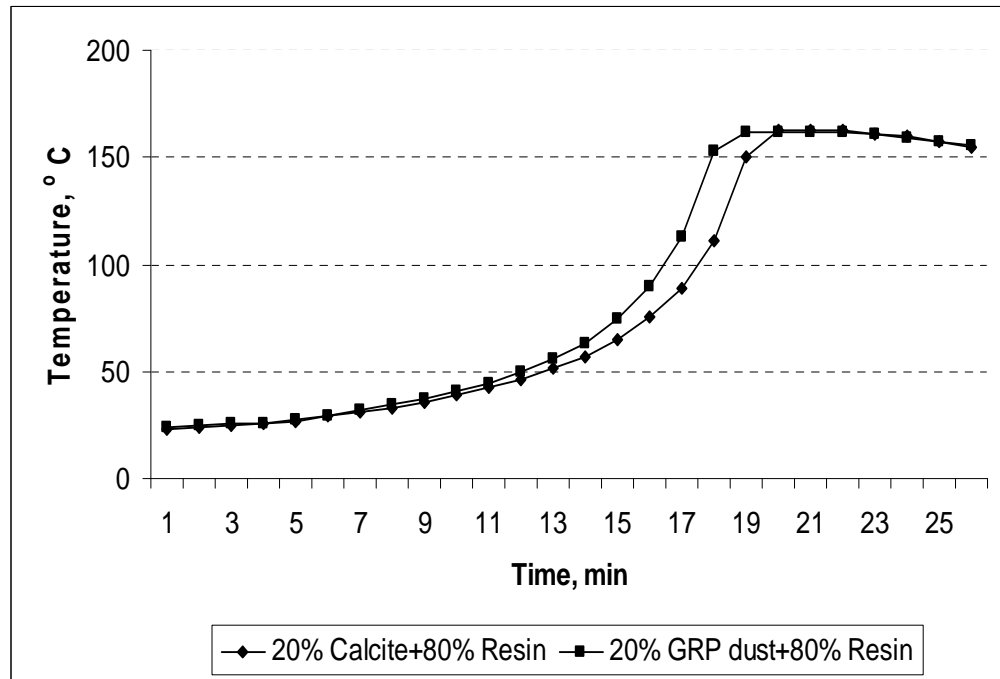


Figure I.3 Exotherm graph for 20% weight of added filler with curing time

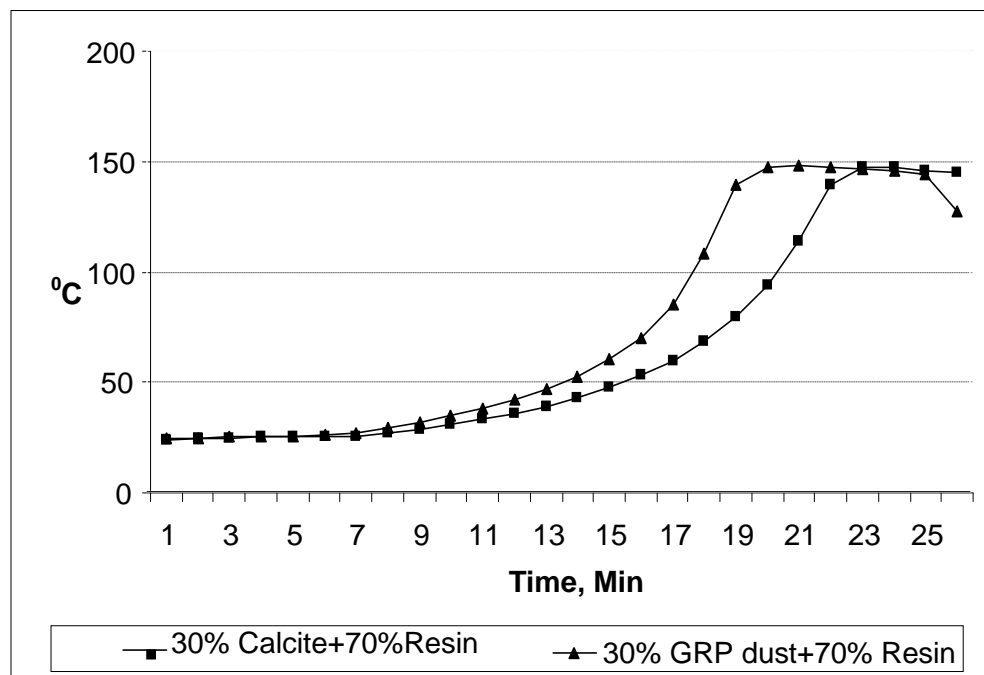


Figure I.4 Exotherm graph for 30% weight of added filler with curing time.

CURRICULUM VITAE

PERSONAL

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EDUCATION

02. 2008 - 01. 2010 Ege University Engineering Faculty

Chemical Engineering Department, Master of Science

Thesis: “Studies on recycling of glass fiber reinforced polyester resin composite”

09.1996 – 07.2002 Ege University Engineering Faculty

Chemical Engineering (%100 English, Bachelor’s degree)

WORK EXPERIENCES

02. 2008 - 08. 2008 – Nova Metal Company, Izmir

Technique Sales Manager

- Sale of metals and its auxiliaries, following customer jobs, organisation and quality control documentation

08. 2004 – 03. 2007 – Yesim Textile Factories, Bursa

Specialist of Dying

- Cotton, polyester %100 organic, tencel garment dying, finishing printing processes responsibilities.

- Administration of staff

Process Control Manager

- Quality control of dying and printing processes
- ISO 9001: 2000 Quality Production Management and ISO-EN 14000 Environment Quality Management System are applicated inside the dying production departments

- 5S, Kaizen, Lean Production feasibility and training studies

05. 2003 – 04. 2004 – Reisoglu Yarn Textile Factory, Bursa

Quality Control Chief

- Quality control of finished garments and buying of something needed in the equipment and materials of a business

TRAINING

- 07. 2000 - 08. 2000 Internship, Petkim Petrokimya A.Ş. Polypropilene Plant, Izmir, Turkiye
- 07. 1999 - 08. 1999 Internship, Aromel Cosmetic Factory, Izmir, Turkiye

QUALIFICATION

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- ISO EN 9001: 2000 Quality Production Management, Basic 23- 24.08.2006, Ender Teknik, Bursa, Turkiye (Certificated)
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PROJECTS

-Studies on recycling of glass fiber reinforced polyester resin composite,

MSc. Thesis, Ege University, 2009, Izmir

-Polystyrene Foam Sulfonation, **Diploma Thesis**, Ege University 2002, Izmir

-Acrylic Acide Production, **Design Project**, Ege University 2002, Izmir

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COMPUTER SKILLS

Word, Excel, Power Point, MATLAB, Visual Basic, Chemcad, Internet Tech.

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English(Good), Italian(Low)

INTERESTS

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