

THERMOSET POLYESTER WITH PHASE CHANGEABLE FILLERS
FOR HEAT STORAGE

by

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B.S. in Chem., İstanbul Üniversitesi, 1997

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science
in
Chemistry

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ACKNOWLEDGMENTS

First of all, I am deeply grateful to Prof. Dr. Selim H. Küsefođlu, who assisted and encouraged me a lot during this work, for his academic support, and friendly tolerance. I want to thank him for his friendly manners both as an advisor and as a person

I would like to express my sincere gratitude to Prof. Nihan Nugay for her valuable advice and comments I also thank to Prof. Sabri Altıntaş for his support and advice.

I would also like to thank all members of Chemistry Department for their encouragement and friendship. Special thanks to Hüseyin Esen, Mustafa Yılmaz, Sinan Şen, and Tarık Eren for their help and intimate friendship.

I also thank to Egemen Burak Öncel, Haluk Laçın, Nuran Aydemir, Orçun Temizkan, and Özgür Ergül, for their infinite support and invaluable friendship.

My last thanks go to my family for their invaluable assistance and support.

ABSTRACT

THERMOSET POLYESTER WITH PHASE CHANGEABLE FILLERS FOR HEAT STORAGE

In this study, emulsions and sols of unsaturated polyester, containing phase changeable fillers (PCM) PEG-4000, paraffin, and Wood's metal, were prepared. Unsaturated polyester was the continuous phase and fillers were the discrete phase. These fillers were well distributed and dispersed in unsaturated polyester. Emulsions and sols containing different proportions of fillers were prepared, and the continuous phase was cured with initiator, methyl ethyl ketone peroxide (MEKP) and accelerator; cobalt naphthanate. After curing, the product becomes a thermoset polyester composite which was filled with homogenously distributed PCMs. Mechanical, thermal properties, and surface hardness of cured material were examined. DMTA (Dynamic Mechanical Thermal Analysis), DSC (Differential Scanning Calorimeter), SEM (Scanning Electron Microscope), and shormeter were used for these purposes. The mechanical properties of cured resins vary with PCM content. Paraffin causes sharp decreases in mechanical properties. Reduction of mechanical properties is sudden at 5 per cent paraffin content, then reduction gradually goes on at slower rate as the paraffin amount increases. PEG-4000 also causes decrease in mechanical properties but they are not as sharp as in paraffin case. Wood's metal does not cause a sharp reduction in mechanical properties at low percentages. In paraffin and Wood's metal filled samples, the filler is a load bearing component. At phase change temperatures of the fillers, the samples show observable changes in dynamic mechanical properties. Maximum working temperatures of cured samples also decrease with increasing filler amount. Neat polyester does not show any melting transition, however, paraffin and Wood's metal filled samples show melting transitions. PEG-4000 filled samples do not show melting transition. Around the melting point of fillers materials absorbs a certain amount of heat. Except PEG-4000 filled samples, paraffin and metal filled samples show an endotherm around the melting point of

filler while materials themselves show no indication of melting externally and retain their physical shape.

ÖZET

ISI DEPOLANMASI İÇİN FAZ DEĞİŞTİREBİLEN DOLGULU TERMOSET POLYESTER

Bu çalışmada, faz değiştirebilen dolgular (PCM (PEG-4000, parafin ve Wood's metal)) kullanılarak, duymamış polyester içinde sollar ve emülsiyonlar elde edildi. Bu emülsiyon ve solların sürekli fazı doymamış polyesterdir. Faz değiştirebilen bu maddeler polyester içinde homojen ve küçük parçacıklar halinde dağıtılmış durumdadır. Değişik yüzdelerde dolgu içeren emülsiyon ve sollar hazırlandı ve sürekli faz metil etil keton peroksit (MEKP) ve kobalt naftanat yardımı ile kürlendi. Kürlenmeden sonra içinde homojen şekilde dağılmış faz değiştirebilen homojen dolgulu termoset polyester elde edildi. Kürlenmiş termoset materyalin termal, mekanik özellikleri ve yüzey sertliği incelendi. DMTA (Dinamik mekanik termal analiz), DSC (Diferansiyel tarayan kalorimetre), Shoremeter (Şormetre) ve SEM (Taramalı elektron mikroskopu) cihazları bu amaçla kullanıldı. Kürlenmiş polimerin mekanik özellikleri PCM miktarıyla değişti. Parafin mekanik özelliklerde ani düşüslere yol açtı. Yüzde 5 oranında parafin dolgulu polyesterde bile ani düşüsler gözlemlendi fakat sonra parafin miktarındaki artış mekanik özelliklerde ani düşüslere yol açmadı. PEG-4000 de mekanik özelliklerde düşüşe yol açtı ancak bu düşüslere parafin dolgulu polyesterdeki kadar aşırı olmadı. Wood's metal düşük oranlarda mekanik özelliklerde gözle görülür düşüslere yol açmadı. Parafin ve Wood's metalin yük taşıdığı gözlemlendi. Dolguların fazlarını değiştirdiği sıcaklıklarda dinamik mekanik özelliklerin değiştiği gözlemlendi. Kürlenmiş örneklerin maksimum çalışma sıcaklıkları artan dolgu miktarı ile azaldı. Dolgusuz kürlendirilmiş polyester, DSC termogramında herhangi bir erime davranışı göstermedi. Buna karşılık parafin ve metal dolgulu polyester örnekleri, dolguların erime noktaları civarında erime davranışı gösterdi. PEG-4000 dolgulu örneklerde bu davranış gözlemlenmedi. Yine dolguların erime noktaları civarında örnekler belirli oranda ısı absorbladılar. PEG-4000 dışındaki dolgulu örnekler, dolguların erime noktaları civarında kendi fiziksel hallerini koruyarak erime davranışı gösterdiler.

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LIST OF ABBREVIATIONS

| | |
|---------------|-----------------------------------|
| CE 92 N8 | A commercial type of UPE resin |
| CMC | Critical micelle concentration |
| Co Naphtanate | Cobalt naphtanate (catalyst) |
| Cp | Specific heat |
| DMA | Dynamic mechanical analysis |
| DSC | Differential scanning calorimeter |
| E' | Storage modulus |
| E'' | Loss modulus |
| ΔH_f | Heat of fussion |
| HLB | Hydrophilic lipophilic balance |
| MEKP | Methyl Ethyl Ketone Peroxide |
| PCM | Phase change material |
| PEG-4000 | Poly ethylene glycol-4000 |
| SEM | Scanning electron microscope |
| Tan δ | Loss factor |
| Tg | Glass transition temperature |
| UPE | Unsaturated polyester |

1. INTRODUCTION

1.1. The Colloidal State

Thomas Graham in his fundamental paper "Liquid Diffusion Applied to Analysis", showed that substances like certain inorganic salt, sugar, and glycerol, which are readily obtained in a crystalline form, will diffuse through water and certain membranes much more rapidly than substances such as, albumin, gelatin, and the hydrous oxides, which are gelatinous and are obtained in the form of definite crystals with difficulty, if at all. Substances which diffuse rapidly were called crystalloids, and those which exhibit little or no tendency to diffuse were termed colloids, from Greek colla, mean glue [1].

A phase is said to be colloidal when it is sufficiently finely divided in at least one dimension. Strictly speaking, therefore, the term colloid should be used only as an adjective to define a physical system of matter usually made up more than one substance. But for convenience, colloid term is frequently referred to finely divided phase. This is particularly true if we are dealing with colloidal organic materials such as, gelatin, agar, and rubber, which are either non-crystalline or sub-microscopically crystalline [1].

1.1.1. The Colloidal Zone

A colloidal system is a micro heterogeneous or dispersed system of at least two phases, one of which is a finely divided or dispersed phase uniformly distributed in a continuous phase, the dispersion medium (Figure 1.1). Colloidal science concerns systems in which one or more of the components has at least one dimension within the nanometres (10^{-9}) to micrometers (10^{-6}) range [2].

Colloidal system can be divided into three groups on the basis of the size of the particles and colloidal particles are between 0.001 micrometer and 0.1 micrometer. For the most part, particles in the colloidal state consist of aggregates of molecules that are too small to be resolved in the ordinary microscope; ultra microscopes are useful for this purpose.

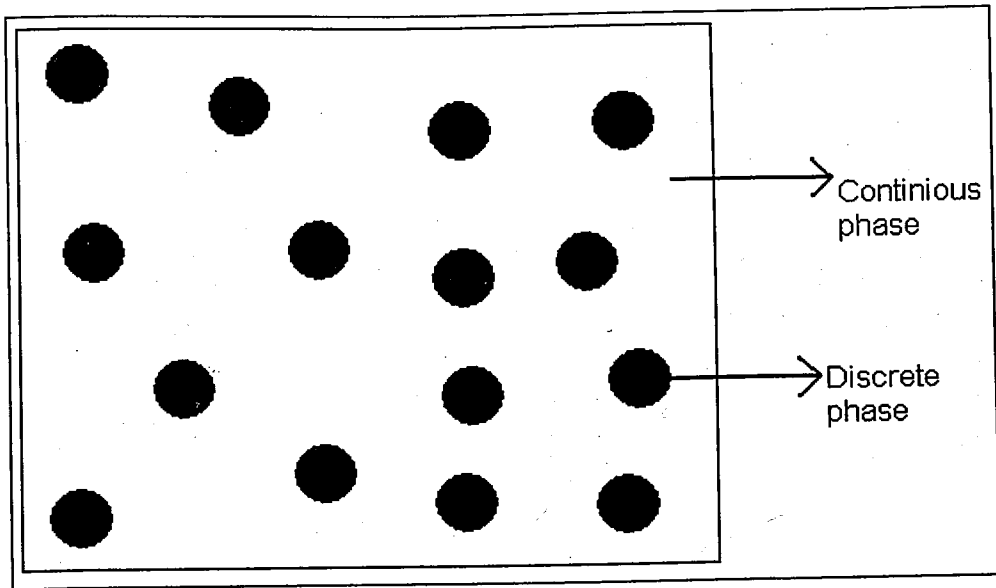


Figure 1.1. Basic representation of a colloidal system

1.1.2. Classification and Terminology

1.1.2.1. Disperse Systems. Classifying colloidal systems on the basis of the states of aggregation (solid, liquid, and gas), Ostwald recognized eight type of systems.[1] These are given in Table 1.

Sol is general term usually used for dispersions of solid in liquid, solid or gaseous media. If the dispersion medium is water, the system is termed as a hydrosol [1]; if the dispersion medium is an organic liquid, it is called an organosol or lyosol. Emulsion is the general term for dispersions of liquid in either liquid or solid media.

1.1.2.2. Difform Systems. The shape of a particle as well as its size determines extent of surface. For example, a sphere may be rolled out into a disk, sheet or film or maybe drawn into a thread of any desired thickness, thereby increasing greatly the extent of surface without subdivision. Ostwald gave the name difformation to extreme distortion which results in a marked increase in specific surface [1].

1.1.2.3. Lyophobic and Lyophilic Systems. Another classification of certain colloid systems is based on the attraction or affinity of the dispersed phase and the dispersion

medium for each other. If the mutual affinity is small, the system is said to be lyophobic, whereas if the mutual affinity is great, the system is lyophilic. If water is dispersion medium, the system is termed hydrophobic or hydrophilic.

Table 1.1. Dispers systems

| Dispersed phase | Dispersion Medium | Name | Example |
|-----------------|-------------------|----------------|------------------------------------|
| Solid | Liquid | Sol | Gold in water |
| Liquid | Liquid | Emulsion | Milk, mayonnaise |
| Gas | Liquid | Foam | Froth of beer, foam on soap |
| Solid | Solid | Solid sol | Gold, ruby glass, alloys |
| Liquid | Solid | Solid emulsion | Milk, quartz, pearl, opal |
| Gas | Solid | Solid foam | Lavas, pumice |
| Solid | Gas | Solid aerosol | Smoke, NH_4Cl fume |
| Liquid | Gas | Liquid aerosol | Fog, cloud, mist |

1.1.3. Preparation of Colloidal Systems

There are two fundamentally different ways in which colloidal dispersions can be formed, either by breaking down bulk matter to colloidal dimensions (dispersion methods) or by building up molecular aggregates to colloidal sizes (nucleation or condensation methods) [3].

- Dispersion methods are:
 - Comminution
 - Emulsification
 - Suspension and aerosol methods

- Condensation methods are:
 - Nucleation and particle growth
 - Emulsion or dispersion polymerization

1.1.4. Stability of Colloids

A most important physical property of colloidal dispersions is the tendency of particles to aggregate. Encounters between particles dispersed in liquid media occur frequently and the stability of dispersion is determined by the attraction between the particles during encounters [2].

The principal cause of aggregation is the Van der Waals attractive forces between the particles, which are long-range forces. To counteract these and promote stability, equally long-range repulsive forces are required. Solvation tends to be too short-range; however, the molecular ordering associated with the solvation can propagate several molecular diameters into the liquid phase and may exert some influence on stability [4]. The principle stabilising options are electrostatic (i.e. the overlap of similarity charged electric double layers) and polymeric. Polymer and/or surfactant additives can influence stability by a variety of mechanisms and the overall situation is very complicated [2]. Ideally, lyophobic sols are stabilized entirely by electric double-layer and as such, present colloidal stability at its simplest. If the system contains lyophilic material, using protective agents and polymeric materials, which are absorbed on the surface of colloidal particle and provide steric stability, would stabilize the colloidal system.

1.2. Surfactants

Surfactant is an abbreviation for surface-active agent. Coined in 1950, surfactant has become universally accepted to describe organic substance with certain characteristic

features in structure and properties [5].

Surfactants are amphiphilic molecules. They are composed of groups of opposing solubility tendencies, one, which is soluble in specific fluid (the lyophilic part) and another, which is insoluble (the lyophobic part). When the fluid is water one usually talks about the hydrophilic and hydrophobic parts respectively. The hydrophilic part is referred to as the head group and hydrophobic part as the tail (Figure 1.2).

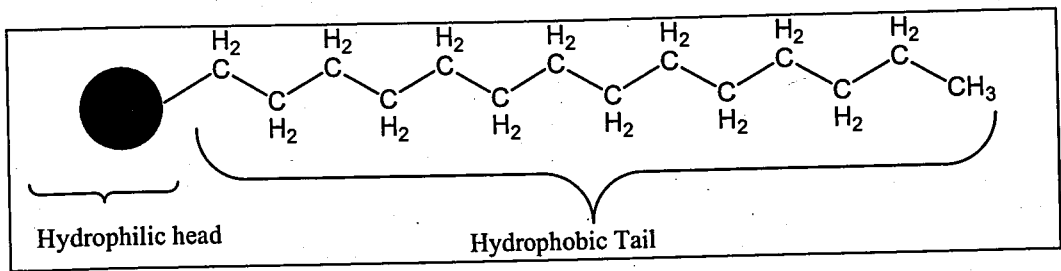


Figure 1.2. General structure of surfactant

Surfactants are soluble in at least one phase of a liquid system. Surfactant and ions form oriented monolayers at phase interfaces. When the concentration of surfactant in the bulk of solution exceeds a limiting value, which is called critical micelle concentration (CMC), micelles, which are aggregates of molecules or ions of surfactants, are formed. Surfactants exhibit combination of cleaning, foaming, solubilizing, and dispersing properties [6]. Surfactants are classified depending on the charge of surface-active moiety usually the larger part of the molecule. Thus, surface-active agents can be divided into five groups. These are anionic, cationic, non-ionic, zwitter ionic, and semipolar surface-active agents. In anionic surfactants, this moiety carries a negative charge, as in soap [6].

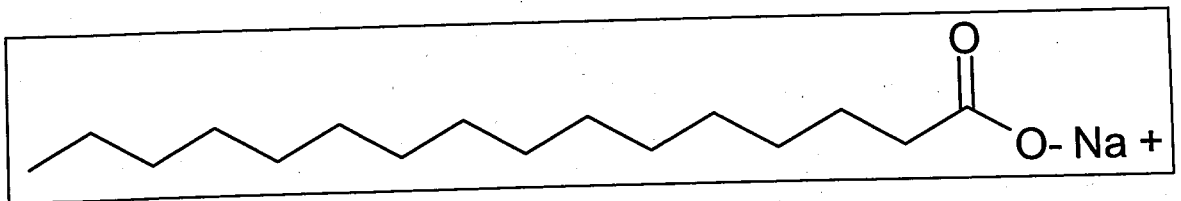


Figure 1.3. Structure of sodium stearate

In cationics surfactants, the charge of head group is positive as seen in Figure 1.4.

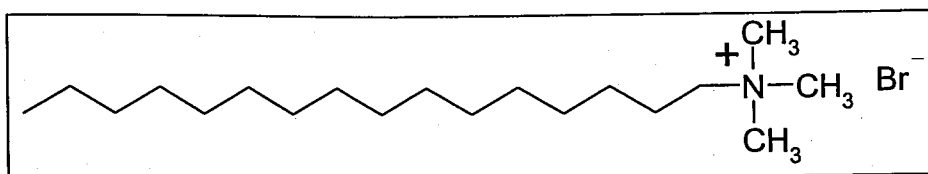


Figure 1.4. Structure of octadecyl three methyl ammonium bromide

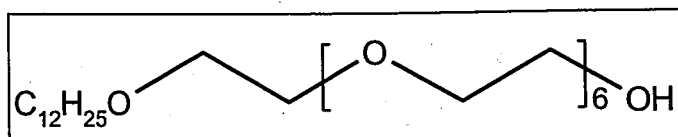


Figure 1.5. Structure of polyhexaethyleneglycol mono lauryl ether

In non-ionic surfactants, as the name implies, there is no charge on the molecule; the solubilizing contribution is supplied by a chain of ethylene oxide groups (Figure 1.5).

In zwitter ionic surfactants, solubilization is provided by the presence of positive and negative charges in the molecule.

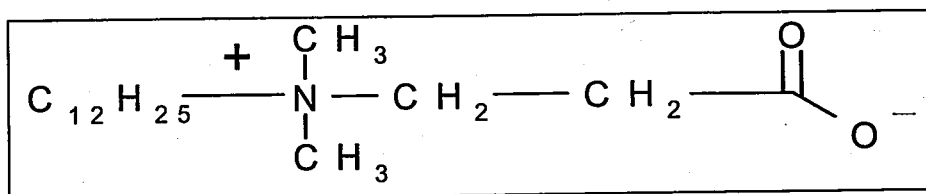


Figure 1.6. Structure of zwitterionic surfactant

In semipolar surfactants, molecule carry positive and negative charge but structure is different from zwitter ionics.

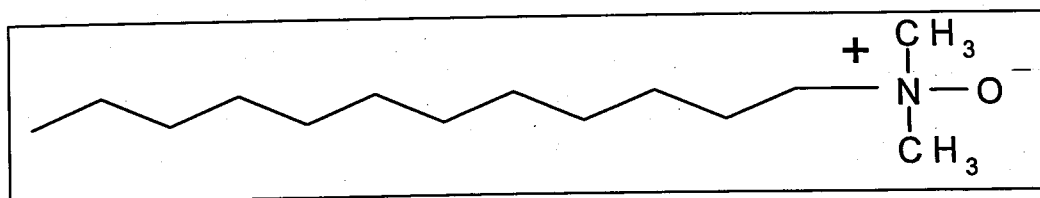


Figure 1.7. Structure of somipolar surfactant

When a material is used to store and deliver heat reversibly by melting and freezing, it is called as “Phase Change Material” (PCM). PCMs can store much greater heat amounts at small changes in temperature. For example, PCM 72, which is commercially available from Merck, on a weight basis can store four times more heat than water and 10 times more than stone or brick in the temperature range from 70 to 80°C.

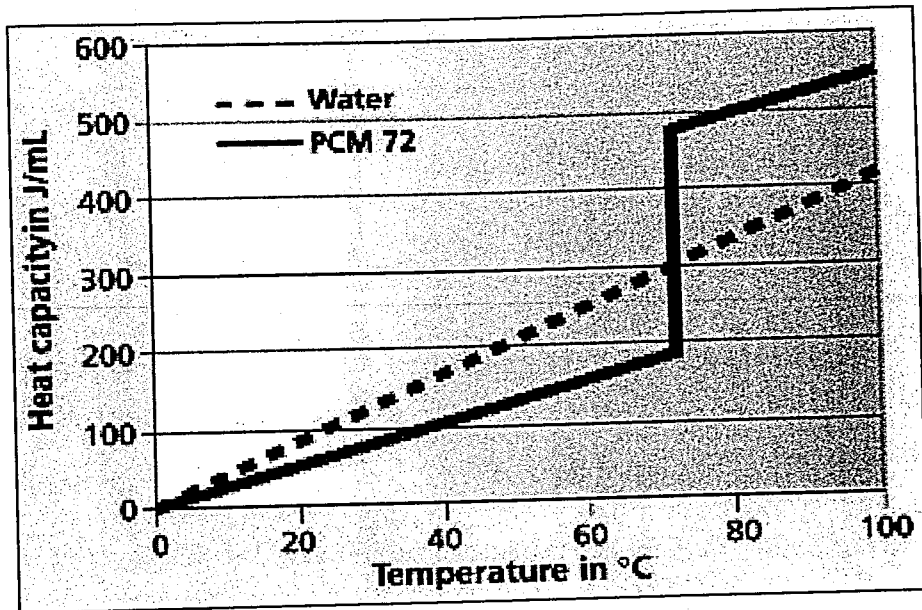


Figure 1.9. Heat capacity versus temperature graph [7].

1.3.1. Selection Criteria for PCMs

Particularly suitable materials for heat storage and re-use of latent heat are inorganic salts and salt mixtures and some organic substances such as, paraffins. These substances must meet certain criteria in order to be used in technical applications.

Melting point: Depending on the application, the PCM must have the appropriate melting point.

Heat Storage Capacity: The PCM must be able to store a sufficient amount of heat (per unit weight) to work efficiently. In addition to a high heat of fusion (in J/g), a high specific heat C_p (in J/gK) and low density beneficial are for a large heat storage capacity.

Important for use in closed systems is very small volume difference between solid and liquid phase and low vapor pressure.

The above described phase transitions for heat storage must be reproducible and must have a high cyclical stability. The PCM must remain both physically and chemically stable during the heat transfer process. It must melt homogeneously at a defined temperature (congruent melting). A separation of the ingredients or decomposition must not take place.

The PCM must possess a good heat conductivity to insure that the heat be observed and emitted quickly.

The corrosiveness of the PCM to surrounding materials must be low.

Further criteria for suitability of PCM are such properties as environmental safety, recyclability, non-toxicity, and low price [7].

1.3.2. Some Applications of PCMs

1.3.2.1. Application in Textile. Since the introduction of water-proof and permeable materials, the importance of functional textiles is growing more and more. A new attempt to improve wearing comfort of ski clothing uses PCM: if the clothing is worn indoors or if the wearer is active, The PCM absorbs heat by melting and cools the athlete. When the athlete is inactive (for example while waiting in line for the ski lift), the PCM emits heat by solidifying and warms the athlete (Figure 1.10) [7].

1.3.2.2. Application in Electronics. Electronic circuitry is extremely sensitive to overheating, which negatively influences both lifetime and reliability of the parts. To date, metal fins are used for heat sinking improving their cooling capacity with additional fans. These constructions have moving parts which can break. The use of PCMs to absorb heat during peak activity is absolutely reliable since no motor or electronic devices are required. The PCM regenerates itself between peaks by emitting the heat with cooling fins. The advantage is a smaller cooling system with a very high reliability and zero running cost [7].

1.3.2.3. Application in Construction Materials. The atmosphere in a room is found comfortable if the temperature stays constant. For this reason, homes with very thick walls are found especially comfortable: cool in the summer and warm in the winter. To achieve this comfort with less massive construction, one can use PCMs. By absorbing heat during daytime (i.e. during sunshine) and releasing heat at night, temperature of a house can be regulated with PCMs [7]. In fact PCM filled walls and bricks are commercially available in some countries.

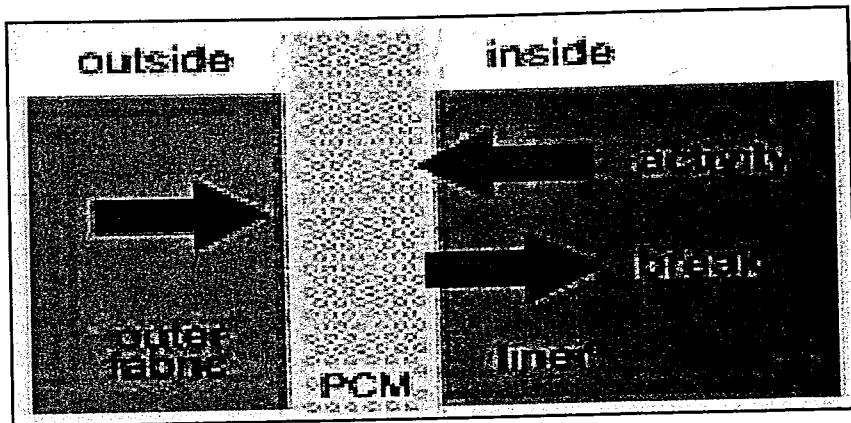


Figure 1.10. Application of PCM's in fabric [7]

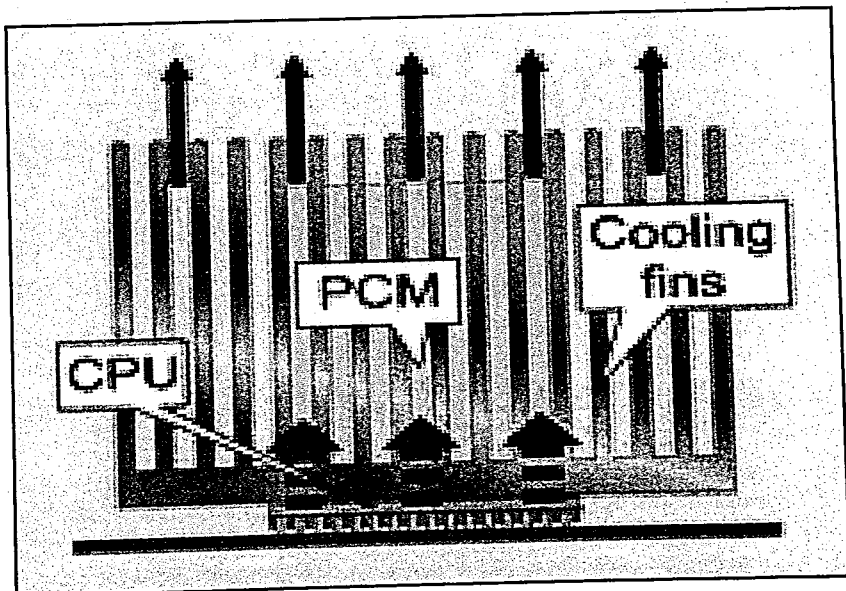


Figure 1.11. Application of PCM's in electronics [7]

1.3.2.4. Application in Solar Heating. Solar energy is not available at all times, and therefore solar installation require an intermediary storage of the energy for heating or warm water. The advantage of PCMs in this application is the use of smaller volume boiler in a higher efficiency due to a lower temperature difference between loading and discharging of the energy. Latent heat storage can also be implemented in conventional heating systems [7].

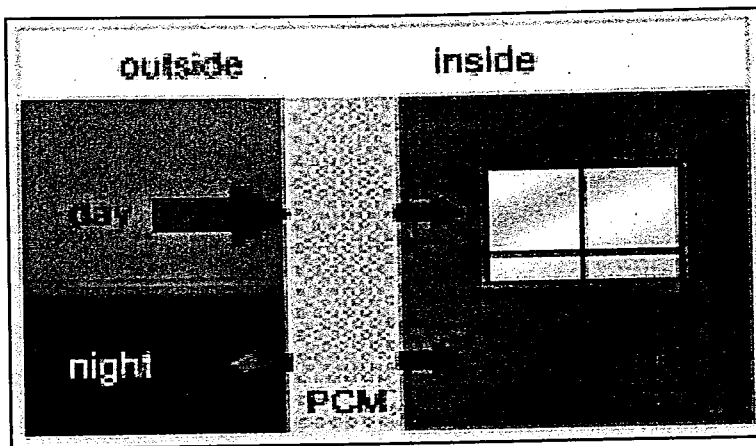


Figure 1.12. Application of PCM's construction materials [7]

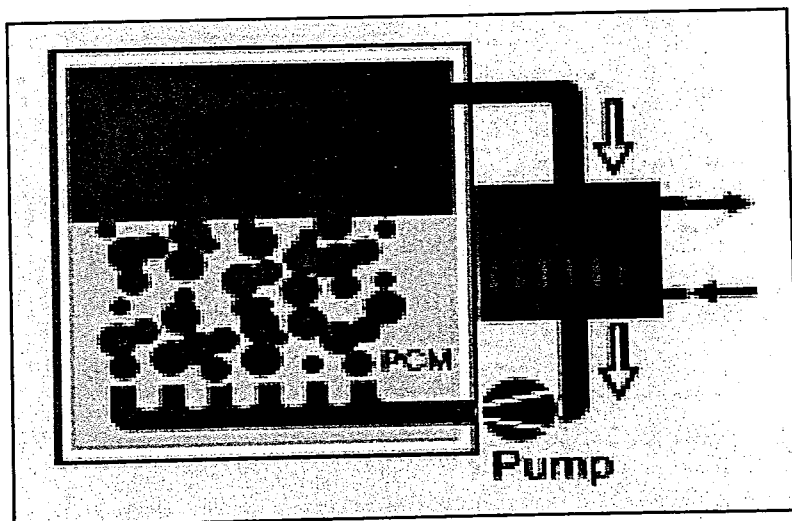


Figure 1.13. Application of PCM's for solar heating [7]

1.3.2.5 Usage in Food Service. A similar concept is used in a commercially available dinner plate. The plate which has a void inside filled with PCM material is first heated in

an oven, and then keeps the food placed on it warm for an extended period. These plates are used in hospitals and schools where a large number of people need to be served in a short time.

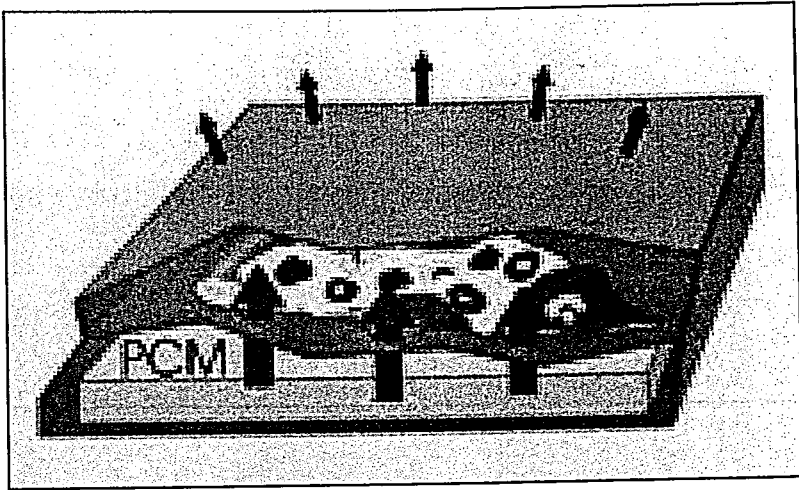


Figure 1.14. Usage of PCMs for food service [7]

1.4. Fillers and Reinforcements

Fillers are defined as rigid, solid materials added to plastics. Most materials are made from inorganic and powdered and cheap materials and therefore lower the price of the filled plastics. Fillers have much higher moduli than the polymer they replace and, therefore, produce specific improvements in certain mechanical or physical properties and are thus also known as reinforcing fillers. Some fillers form chemical bonds with the material to be reinforced, carbon black, for example, produces cross-linking in elastomers by means of radical reactions.

Other fillers act mainly through the volume that they take up. In the presence of the filler particles, the chain like polymer molecules cannot assume all the conformational positions that are possible and gain rigidity. The polymer segments attached to the filler surface by secondary or primary valence bonds in turn cause a certain immobilization of adjacent segments and a possible orientation of the polymer matrix.

The zone at the filler surface, whose structure would appear to be ordered, thus causes a stiffening of the material as a whole. The lower deformability and higher strength are also due to this composite nature.

The third mode of action of active fillers results from the fact that when the polymer molecules are subject to stress with absorption of energy, they can slide off the filler surface. The impact energy can thus be more uniformly distributed and impact strength increased as in the case of unplasticized PVC/Calcite system. In some cases, microcraze formation that absorbs the impact energy at the filler/polymer interface is also facilitated [8].

1.4.1. Properties of Filled and Reinforced Plastics

The main difference between inert and reinforcing fillers lies in the fact that modulus of elasticity and stiffness is increased to a greater or less extent by all fillers, whereas tensile strength can only be appreciably improved by a fiber reinforcement. Heat deflection temperature, i.e. stiffness at elevated temperatures, cannot be increased by spherical additives to the same extent as by fiber reinforcement. On the other hand, fillers in flake form, such as talc or mica, likewise produce a marked improvement in these values.

- The use of extender fillers can result in the following changes in the properties of plastics:
 - Increase in density
 - Increase in modulus of elasticity, as well as in compressive and flexural strength (stiffening),
 - Lower shrinkage,
 - Increase in hardness and improvement in surface quality,
 - Increase in heat deflection temperature and lowering of the temperature dependence of the mechanical properties, there being generally no improvement in mechanical and physical properties compared with unfilled polymers,
 - Cost reduction

- Reinforcing fillers, on the other hand, produce the following improvements in plastics:
 - Increase in tensile stress at break as well as in compressive and shear strength,
 - Increase in modulus of elasticity and stiffness of the composite material,
 - Increase in heat deflection temperature and lowering of the temperature dependence of the mechanical values,
 - Lower shrinkage
 - Improvement in creep behaviour and bend-creep modulus, reduction in the viscoelastic yield under load; there is also a partial improvement in impact strength.

Disadvantages of the reinforcing fillers are mainly attributable to the generally anisotropic (directional) effect of the reinforcement and an increase in water absorption.

Two discrete phases are always present in reinforced plastics. The discontinuous filler phase should exhibit higher tensile strength and a higher modulus of elasticity than the polymer matrix, whereas the continuous plastic phase should possess higher elongation at break than the filler. For this reason fibers are particularly suitable as reinforcing agents [8].

1.4.3. Application Criteria for Fillers in Plastics

A large number of different aspects have to be taken into account when employing fillers, e.g.;

- Optimum particle distribution curve,
- Possible catalytic activities at the filler surface
- Dispersability and linkage with plastic matrix
- Abrasive action of the filler in processing machines
- Problems of industrial safety due to dust etc.
- Cost

An important criterion of a filler and/or reinforcement is cost. Reinforcing a polymer is only justified when a distinct improvement of mechanical properties or cost reduction compared to the non-reinforced base polymer is found, or when a specific combination of properties is not achievable by other means [8].

1.5. Unsaturated Polyester (UPE)

An ester is a compound which has the structure $R-COOR$. For the purposes of this chapter, polyesters are defined as polymers containing recurring $-COO-$ groups in the main chain [9].

Unsaturated polyesters, also called polyester resins, are based on macromolecules with a polyester backbone in which both a saturated acid, such as phthalic, isophthalic, adipic or azelaic (Figure 1.17), and an unsaturated acid, such as maleic anhydride or fumaric acid (Figure 1.18) are condensed with a dihydric alcohol. As in other condensations, water needs to be removed from the reaction mixture to achieve reasonable molecular weights, typically between 1500-5000 daltons. A three-dimensional structure is produced by cross-linking this polyester backbone, through the unsaturated acid component, with a reactive diluents, most commonly styrene.

The degree of cross-linking can be controlled through the concentration of unsaturated acids or unsaturated glycols. The length of cross-links can be controlled to some degree by concentration and type of cross-linking reactive diluents employed. Rigidity can be introduced by the use of aromatic acids or glycols, and a high degree of cross-linking.

Other compounding ingredients that may be used include curing agents, foaming agents, additives that improves adhesion to fillers and fibers, etc. [10].

1.5.1. Raw Materials

A general purpose linear unsaturated polyester is prepared commercially by the reaction of a saturated diol, which can be ethylene glycol, propylene glycol, or a mixture of

these glycols with other glycols, with a mixture of an unsaturated and a saturated dibasic acids, which can be phthalic acid, isophthalic acid or linear dibasic acid (Figure 1.16). Unsaturated acid provides sites for a subsequent cross-linking; the function of the modifying acid is to reduce the number of reactive unsaturation along the polymer and hence to reduce the crosslink density and brittleness of the final product. In addition those monomers, diluent solvents, catalysts, inhibitors, accelerators are used in unsaturated polyesters [11].

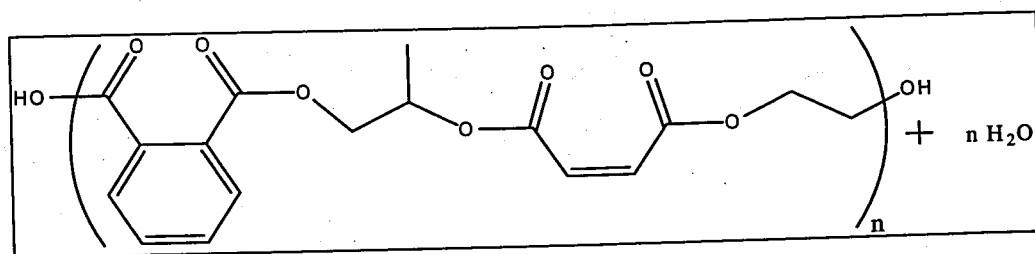


Figure 1.15. General structure of unsaturated polyester

1.5.2. Preparation of Linear Unsaturated Polyesters

Linear unsaturated polyesters are prepared batch-wise by heating a mixture of the appropriate diacids and dihydroxy component in a reactor and removing water by downward distillation. A typical formulation for general-purpose polyester might be as the following; propylene glycol is 100, maleic anhydride 72, phthalic anhydride is 54 parts by weight.

The molar ratio of ingredients shown above is 1, 2: 0,67: 0,33; the excess of glycol is to allow for loss during the reaction and to restrict the molecular weight of the polymer. The mixture is heated at 150-200 °C, 6-16 hours and water is continuously distilled from the reactor. In order to prevent discoloration, the reaction is carried out in an inert atmosphere of either carbon dioxide or nitrogen.

Heating is continued until the average molecular weight of the polyester reaches about 1000-2000. The polymer is then cooled to about 90°C and pumped into a blending tank containing Styrene. In a general-purpose material, the weight of styrene is about half

of the polymer. The blend, (which is commonly referred to as "polyester resin"), is then allowed to cool to room temperature to give a colorless liquid of about 400cps viscosity [9].

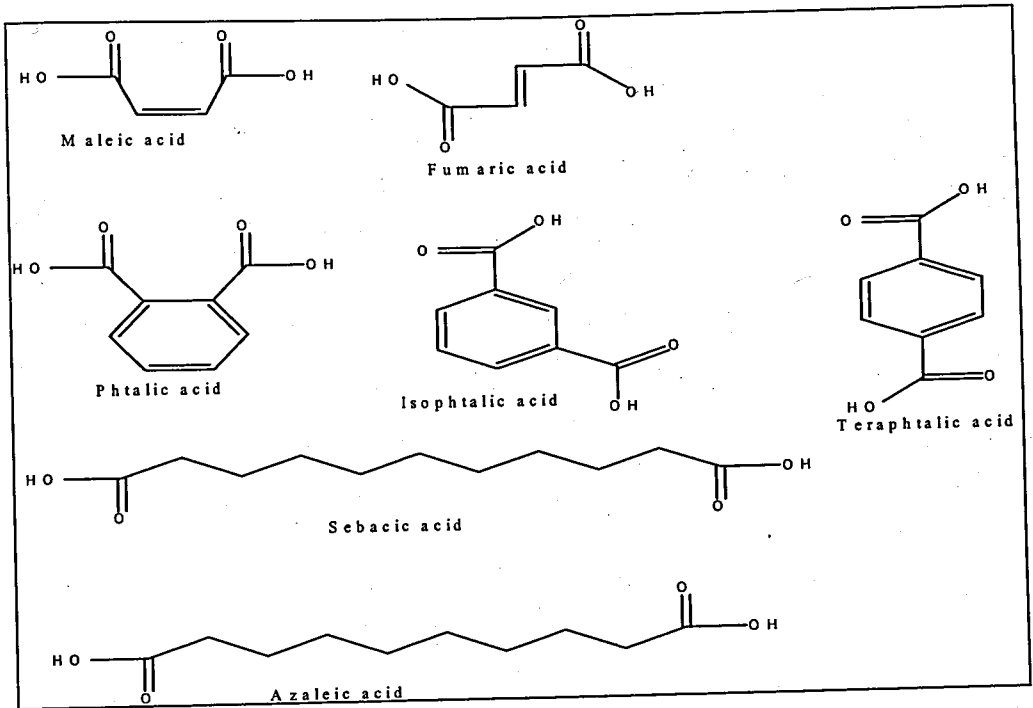


Figure 1.16. Structure of some acids that are used in UPE

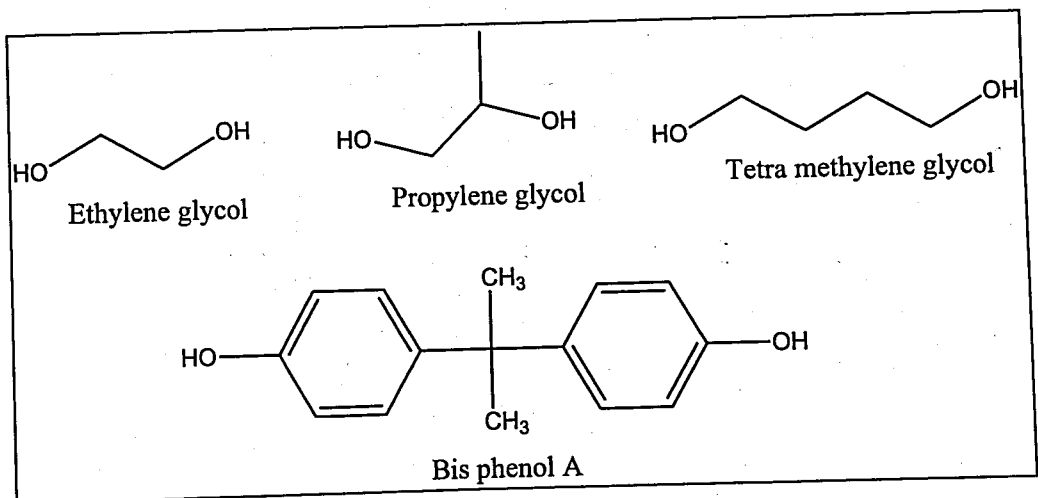


Figure 1.17. Structure of some diols that are used in UPE

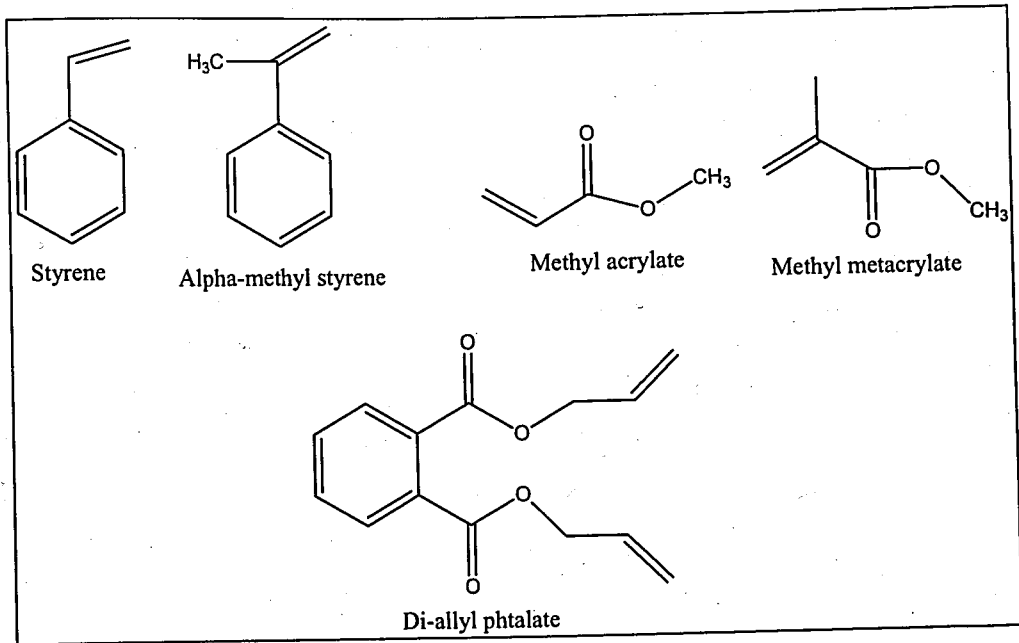


Figure 1.18. Structure of some cross-linking monomers that are used in UPE

1.5.3. Cross-linking

The cross-linking of unsaturated linear polyesters involves the reaction of the unsaturated sites in the polymer chain with a vinyl-type monomer. This reaction is analogous to conventional vinyl copolymerisation and proceeds by an essentially similar mechanism. The cross-linking reaction takes place after the UPE is in the shape of the final article that is manufactured and leads to solidification of UPE to a rigid, durable, load bearing material.

Resins which are “cured” in a mould to a solid product by chemical reaction are called “Thermoset resins”. Two types of initiating systems are commonly employed for this reaction, one is effective at elevated temperatures and other is effective at room temperature [11].

The most important initiators used at elevated temperatures are peroxides that liberate free radicals as a result of thermal decomposition. Benzoyl peroxide (Figure 1.18) is the most widely used one. Mixtures of polyester resin and this type of peroxide are comparatively stable at room temperature but rapidly cross-link at temperatures ranging

from about 70 to 150°C, depending on the choice of peroxide.

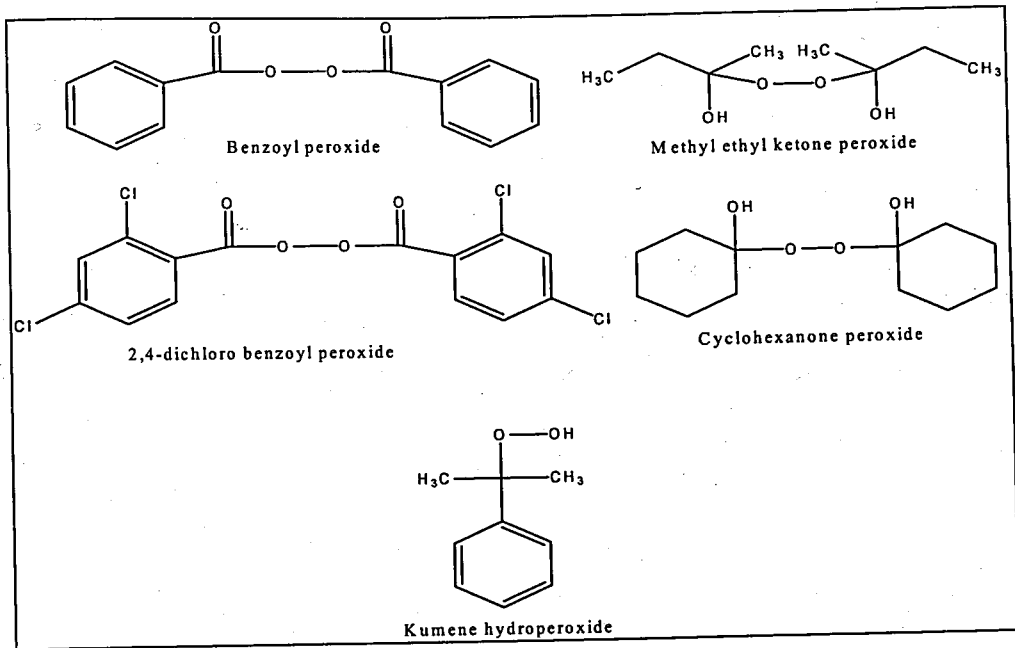


Figure 1.19. Structure of some free radical initiator that are used in UPE cross-linking

Initiating systems, which are effective at room temperature normally, consist of mixtures of peroxy compound and an accelerator (activator). In the presence of the accelerator, the peroxy compound rapidly decomposes without the application of heat into free radicals. The most important peroxy material now used for the “cold” curing of polyester resins is MEKP [11].

The most common accelerators for MEKP are the salts of metals, which exhibit more than one valency. The most widely used metal of this kind is cobalt. In order to be effective as an accelerator, a metal salt must be soluble in the polyester resin. The most commonly used cobalt salts are naphthenates, which are readily soluble. The decomposition of a hydroperoxide (ROOH) by a metal salt such as cobalt naphthenate to give free radicals is shown in Figure 1.21.

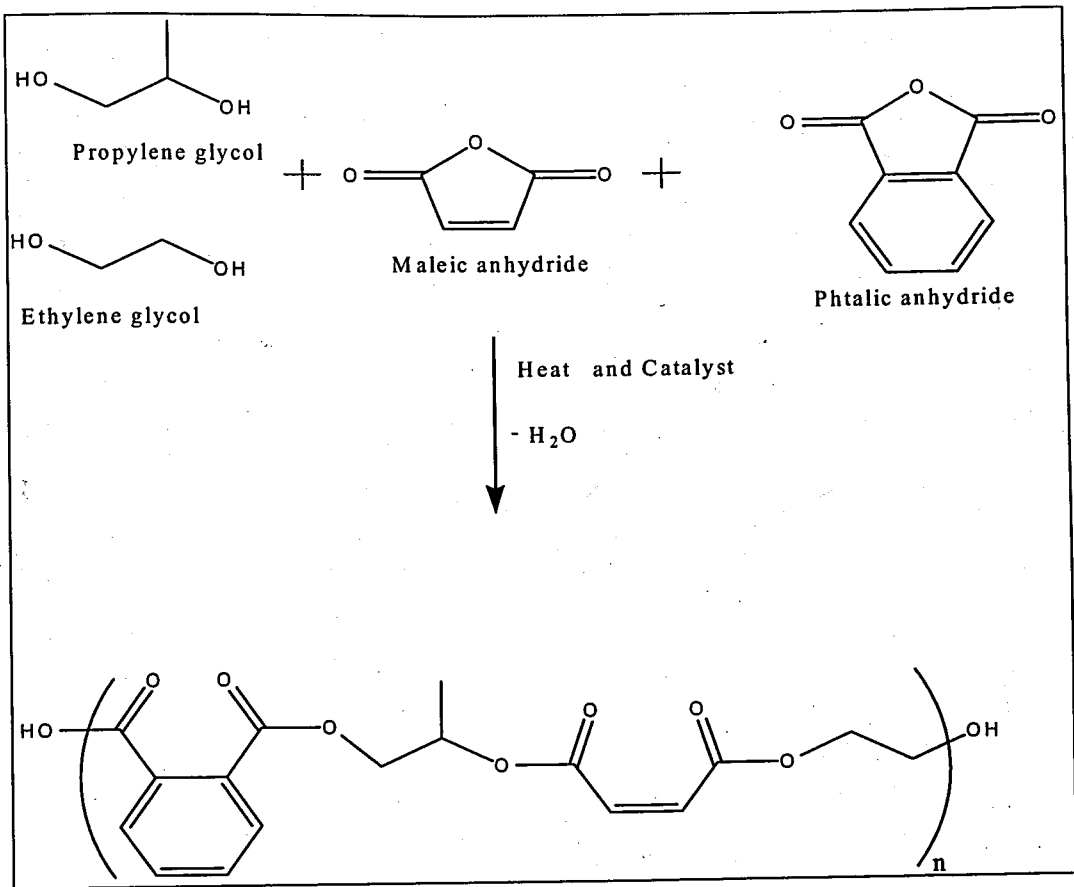


Figure 1.20. Schematic representation of the synthesis of unsaturated polyester

This cycle is repeated until all the hydroperoxide has been decomposed. Cobalt naphthenate-MEKP system is very extensively used in the production of large glass-fibre laminates made by hand lay-up and cured at room temperature.

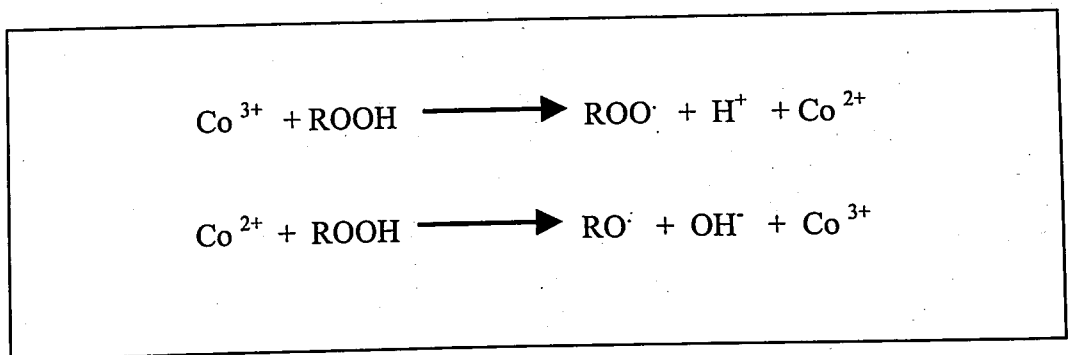


Figure 1.21. Acceleration of the formation of free radicals by cobalt metal

The cross-linking of unsaturated linear polyester by means of a vinyl monomer such as styrene is shown in Figure 1.17.

The cross-linking of linear unsaturated polyesters by vinyl monomers does not involve the elimination of any volatile by-products. Hence it is possible to cure the resin without the application of pressure. Since it is also possible to cure the resins without the application of heat, they are very useful in the manufacture of large structures such as boat hulls, water tanks, water pipes, construction materials, automobile, train and aircraft parts, sports goods etc.

1.5.4. Properties of Cross-linked Polymers

When polyester resins have been cross-linked they are rigid, infusible and insoluble. Polyester resins are mostly used in conjunction with glass fiber and other fillers and the physical properties of final products greatly depend on the type and quantity of glass fiber and other fillers incorporated. Cross-linked polyesters have good heat stability, showing little weight loss up to about 200°C. The mechanical strength of general-purpose materials begins to decline at about 100°C and the maximum service temperature of glass-fibre laminates is about 150°C [11].

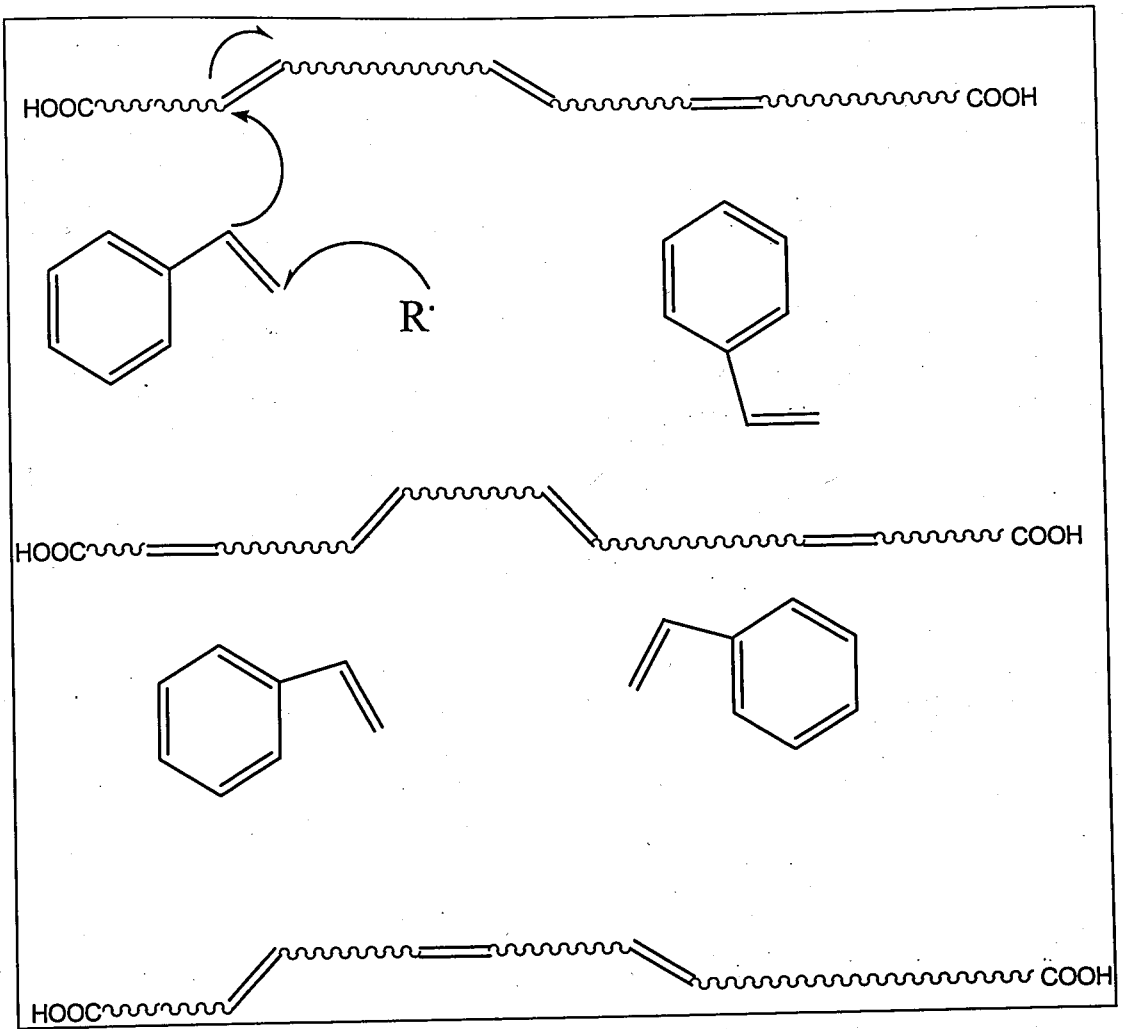


Figure 1.22. Cross-linking mechanism

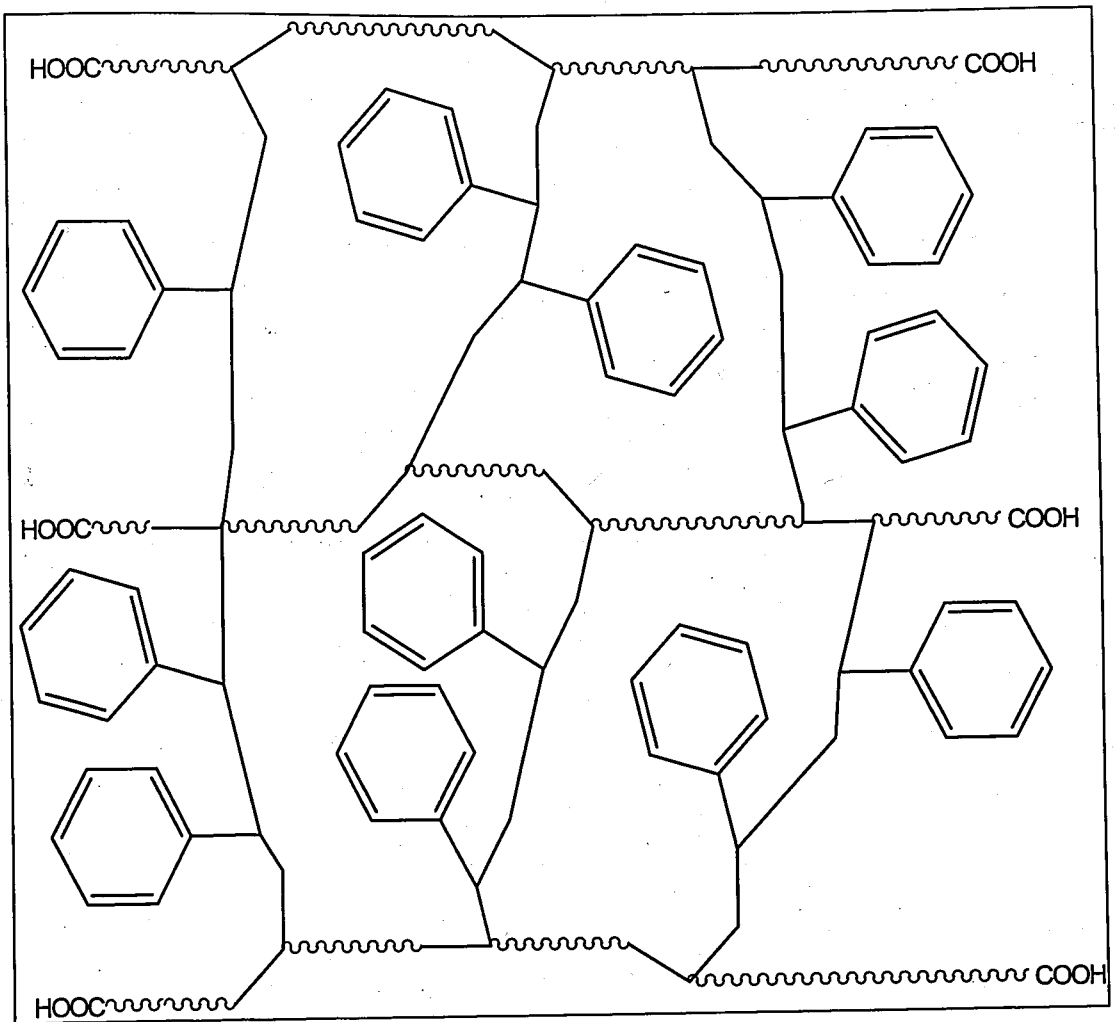


Figure 1.23. Presentation of cross-linked polyester

2. STATEMENT OF THE PROBLEM

The aim of this work is to prepare cross-linked unsaturated polyester, filled with phase changeable fillers. The samples prepared in this way would be the first examples of filled thermoset resin which has filler that can change its phase. Fillers chosen for this study are PEG-4000, paraffin, and Wood's metal.

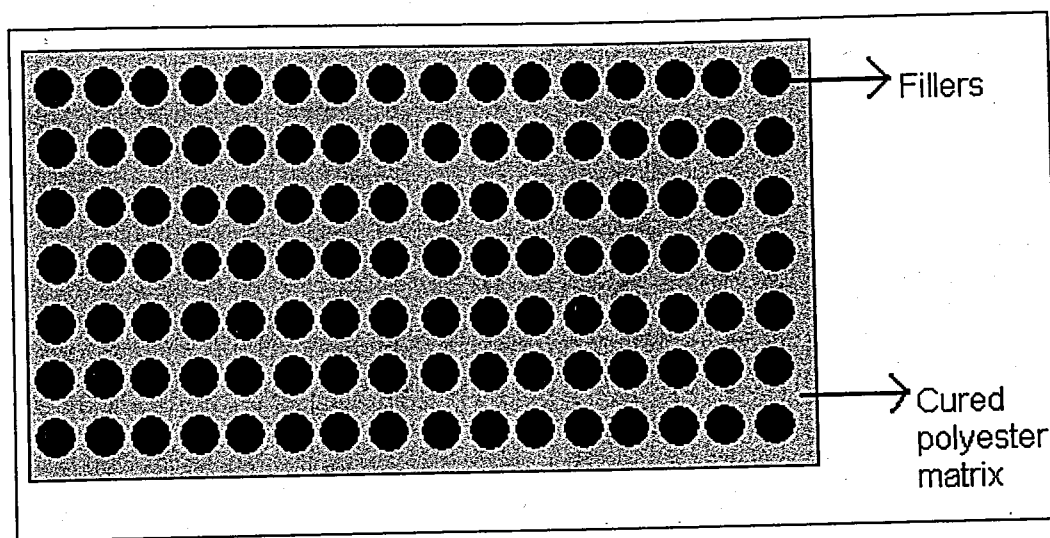


Figure 2.1. Representation of filled polyester

The aim is to first prepare an emulsion or sol having a continuous phase of liquid polyester and discrete phase of PCM by the use of different surfactants. Then the resulting emulsion or dispersion will be cured by peroxide cross-linking of the UPE to obtain a rigid thermoset resin filled with finely divided PCM.

In our experiments, emulsions and sols containing varying proportions of phase changeable filler will be prepared. Their effects on emulsion or sol properties and physical properties of final products will be observed. The mechanical and thermal behavior of such a filled composite around the melting point of filler should be very interesting. Finally, mechanical and thermal properties will be tested by the help of DMTA, DSC. and surface hardness will be measured by shormeter D and emulsion structure was observed by SEM.

The final goal of this project is to produce a rigid, load-bearing, hard material that can absorb large amounts of heat through the melting of the phase changeable fillers, while the material itself shows no indication of melting externally and retains its physical properties. (Figure 2.2). We also plan to observe materials to see if there is an abrupt change in their mechanical properties at the melting point of the filler. DMTA will be used for this purpose.

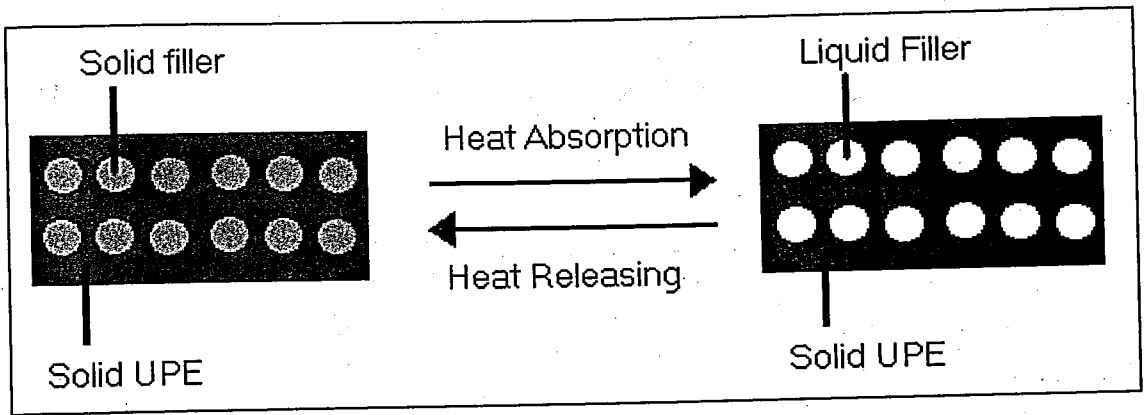


Figure 2.2. Action of PCM filled solid UPE during heating

3. RESULTS AND DISCUSSION

3.1. Sol and Emulsion Preparation

Of the fillers used in this study paraffin and Wood's metal are insoluble in unsaturated polyester and polyethylene glycol is partially soluble. A transition between paraffin, Wood's metal and unsaturated polyester has to be provided by using surfactants.

Traditionally, there are two approaches to emulsification of polymer. One is to modify the polymer so as to include a segment which makes the polymer self emulsifying. The second one is to include an emulsifying agent, which will compatibilize the polyester and filler.

PEG-4000 was too soluble in UPE to give an emulsion. Experiments showed that PEG-Water mixtures containing about 50-60 per cent PEG were sufficiently insoluble to provide an emulsion in UPE. These emulsions are partially stable. Separation time is about 10-20 minutes. Moreover, it was found that an emulsion which contain more than 40 per cent PEG + water mixture could not be prepared due to phase separation.

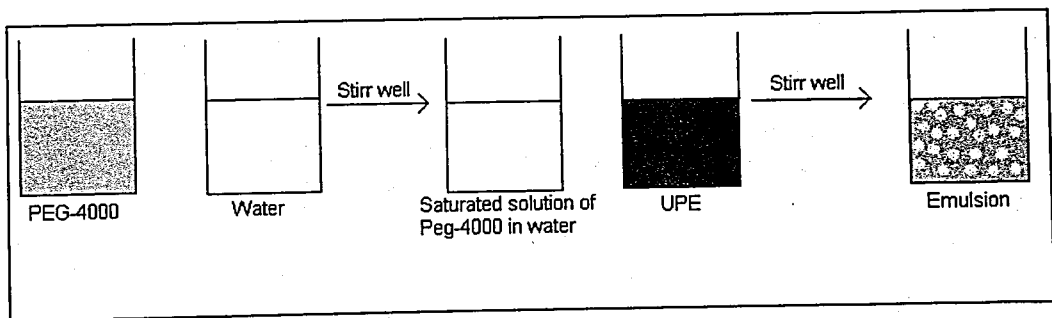


Figure 3.1. General preparation method for PEG-4000 emulsion

PEG acts as both the filler and the emulsifying agent and shows considerable solubility in UPE. Therefore the UPE phase in these composites is not pure UPE but a PEG-UPE solution.

Wood's metal sols were prepared by mechanically powdering the metal and dispersing the powder in liquid UPE. Wood's metal is neither soluble nor compatible in unsaturated polyester. In addition to this, the density of the metal is $9,67 \text{ g/cm}^3$ and that of UPE is $1,1 \text{ g/cm}^3$. Because of the density difference between Wood's metal and unsaturated polyester, adding any surfactant or stirring and mixing are useless methods for preparing stable sols. The fillers always precipitate upon standing. Thus, continuous stirring is necessary to keep metal powder suspended in unsaturated polyester until the polymerization starts at which time medium becomes viscous and density difference is no longer a problem.

Paraffin is a mixture of aliphatic hydrocarbons. Although it is an organic material, it is not soluble in unsaturated polyester. There are two methods to prepare stable paraffin sols in UPE. For both methods, surface-active agent is used and the second method gave more stable and uniform sol so during this study second method was used. In the first method, paraffin is mixed with pine oil, which is naturally occurring abietic acid, and is then dispersed in UPE with sodium stearate surfactant. In the second method, molten paraffin is first emulsified in water with sodium stearate surfactant, solidified by cooling and filtered to give powdered paraffin, which is then used as the filler in our samples. The two methods are shown in Figure 3.2 and Figure 3.3

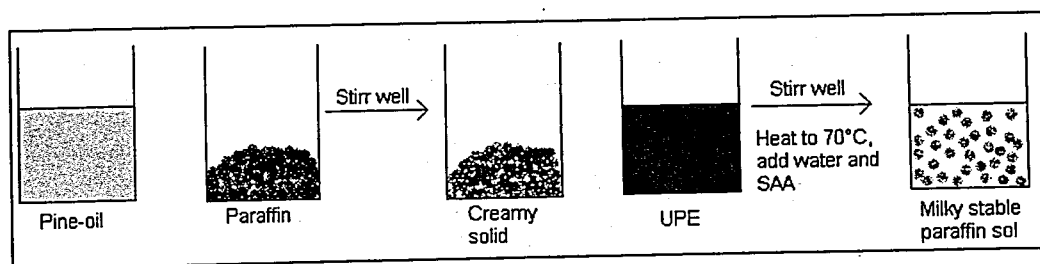


Figure 3.2. First method for preparation of paraffin sols

It was found that pine oil, containing a mixture of abietic acid isomers was a good surfactant for paraffin-UPE emulsions, abietic acid molecules presenting their carboxyl groups to the polyester phase.. Abietic acid is shown in Figure 3.4. It is obvious that in the second method, the surface of the paraffin is changed. The surface is coated with COO^-

groups by using sodium stearate. These groups make paraffin particles more polar and surface of these particles are now compatible with unsaturated polyester (Figure 3.5)

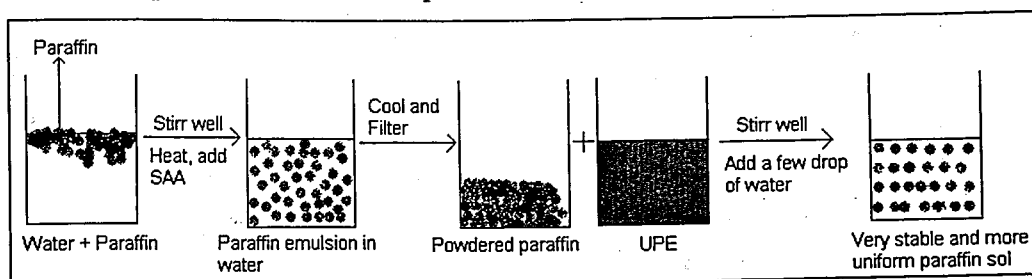


Figure 3.3. Second method for preparation of paraffin sols

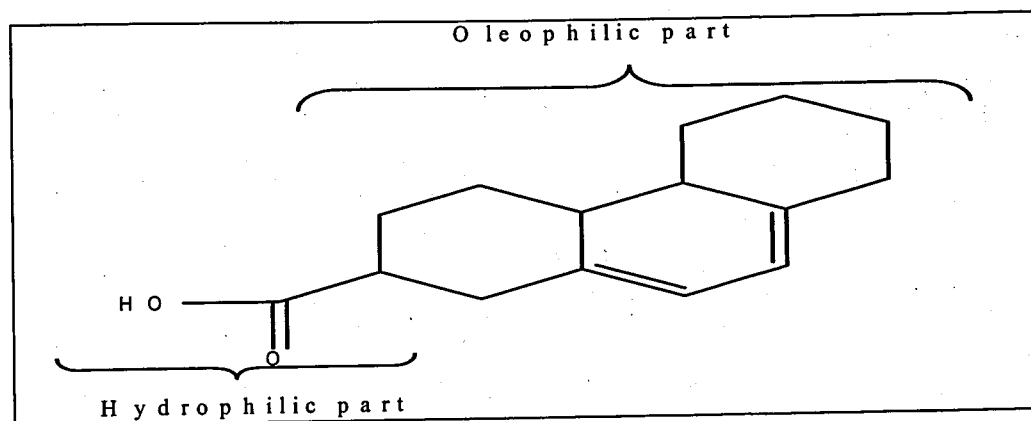


Figure 3.4. Structure of Abietic acid

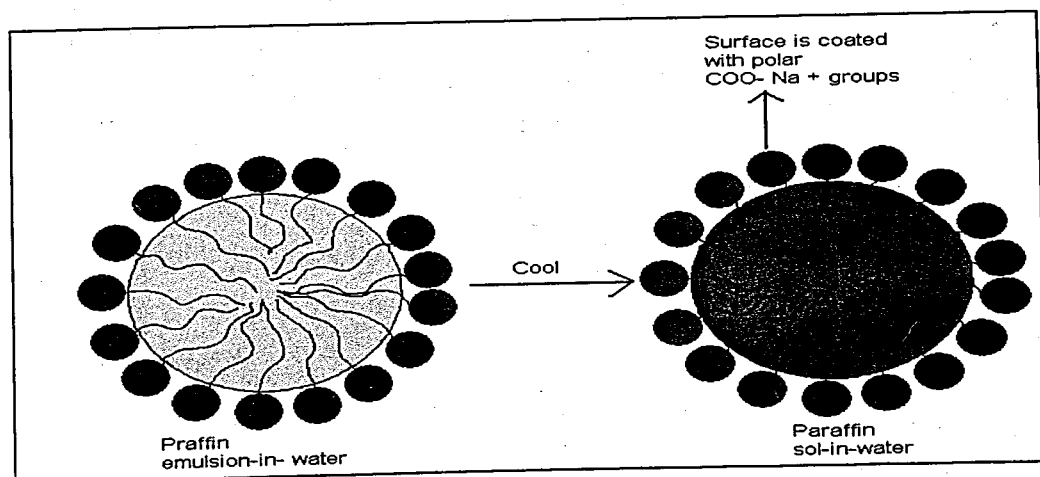


Figure 3.5. Presentation of paraffin particle surface of which is coated COO^- groups

3.1.1. Viscosity of Emulsions and Sols

One of the fundamental properties of emulsions and sols is in the viscosity. Unsaturated polyester resins are generally used in the production methods like; hand lay-up, spray-up, open mold etc. These types of production techniques cannot accept high viscosity. Resins that have high viscosity cannot take the mold details; transferring resin into a mold requires more time, energy and complex machines. Therefore, high viscosity values are undesirable for liquid molding resins.

We found that, as the filler content of emulsions or sols of unsaturated polyester resins increase, viscosity also increases. In fact, this is the general rule for all emulsions and sols having high internal phase content. As the volume ratio of internal phase increases, emulsions and sols exhibit higher apparent viscosity and finally a thick-non-flowing paste is formed. For Wood's metal sols, after 60 per cent concentration sols behave like a paste. However, PEG-4000 emulsions do not show any dramatic increase in viscosity up to 40 per cent. After this point, phase separation takes place. On the other hand, viscosity increases are clearly observed for paraffin sols. After 40 per cent these sols turn to paste. This observed high viscosity sets a limit the internal phase concentration of the samples we made.

3.1.2. Stability of Systems

One of the most important properties of colloidal systems is stability. They are inherently unstable systems and risk of phase separation during storage is high. In our work, the stability required from the emulsion is not very high. As long as the emulsion remained stable while the curing reaction of the UPE proceeded to some extent, homogenous samples could be obtained. For our purpose, instability of emulsions or sols means partial or complete separation of UPE and filler phases because of the difference in their specific gravity.

As the viscosity of emulsion or sols increases, the stability also increases. Finally, it was observed that all the emulsions and sols were reproducible through remixing even after phase separation occurred.

3.1.3. Cross-linking

Unsaturated polyester resins are transformed from a liquid to rigid plastic state by free radical initiation.

As radical source, methyl ethyl ketone peroxide were used, because it is the most widely used initiator with cobalt salts for unsaturated polyesters. The emulsions or sols were cured by using MEKP and Co-naphtanate. Recommended amounts of MEKP on Co-naphtanate for the curing of CE 92 commercial polyester were also used for the emulsions or sols (1 per cent MEKP and 0,5 per cent Co-naphtanate (6 per cent solution in styrene) of UPE content of emulsions or sols). With these amounts of peroxide and accelerator, curing time for CE 92 N 8 was about 10 minutes. However, curing time varied from 15 minutes to 45 minutes depending on the PEG-4000 amount, and paraffin sols cured between 20-40 minutes. For metal sols, curing time was about 5-10 minutes and was independent of metal percentage.

It is known for UPE resins that Co-naphtanate regulates the rate of production of free radicals. One of the most important questions is whether the quantity of cobalt naphatante used is able to control curing time or not. Hence, three samples of PEG-4000 emulsion prepared and containing 30 per cent PEG-4000 + water, were taken and each one was added 1 per cent MEKP. Then, 0,5 per cent, 1 per cent, and 5 per cent Co-naphtanate was added to samples. Each emulsion displayed different curing time. Curing time was taken as the time required for the sample to stop flowing at the tip of rotating stirring rod.

Table 3.1. Change in gelling time with different concentrations of Co-naphtanate

| MEKP | Cobalt 6 per cent | Gelling Time (minute) |
|-------------------|---------------------|-----------------------|
| 1 per cent of UPE | 0,5 per cent of UPE | More than 4 hours |
| 1 per cent of UPE | 1 per cent of UPE | 35-45 minute |
| 1 per cent of UPE | 5 per cent of UPE | 20-30 minute |

Curing time data for emulsions is given in Table 3.1. As seen in Table 3.1, increasing quantity of Cobalt salts increases reaction rate and reduces curing times. To sum up, it is

possible to control the curing times with the amount of catalysts. This has an important commercial application as large parts need a longer time to fill the mould, and cure times have to be long, small parts can be filled faster, and require short cure times.

As a conclusion, it is possible to transfer emulsion or sols of UPE resins from viscous liquid into rigid filled plastics with the aid of free radical producing peroxide; methyl ethyl ketone peroxide, and accelerator; cobalt naphthanate. Moreover, any peroxide catalyst system, which is soluble in oil phase and able to produce free radical at room temperature, would be suitable. As the viscosity of emulsions and sols increases, time necessary for gelling and curing rises. In addition, time necessary for curing is controllable by changing the quantity of accelerator and initiator. Hence, we demonstrated that the fillers used in this study did not interfere with the cure chemistry of the UPE adversely and our samples could be cured easily with known methods. After these preliminary investigations, samples of differing internal phase content were made with each filler and the external phase was cured and the resulting cured resin samples were examined.

3.2. Mechanical Properties of Cured Samples

3.2.1. Dynamic Mechanical Thermal Analysis (DMTA)

Mechanical properties of polymers exhibit a pronounced dependence on temperature. PCMs that were used in this study are PEG-4000 (mp 52-53°C), paraffin (mp 60°C), Wood's metal (mp 68°C). Since, these fillers are capable of changing their phase; if the filler is a load bearing component, the overall mechanical properties of the cured sample should show a change around the melting points of fillers. Therefore, mechanical properties of material under static loading at room temperature may not fully represent its performance. Hence, the cured samples were also investigated in terms of dynamic mechanical behavior at different temperatures.

Dynamic Mechanical Analysis (DMTA) is a thermal analysis technique used to measure changes in viscoelastic response of material as a function of temperature, time or deformation frequency. Our samples were tested at constant frequency as a function of temperature. Samples were scanned at constant strain of 0,01 per cent of the frequency of

1 Hz and heating rate 5 °C/min. Dynamic moduli (E' , E'') and $\tan\delta$ (E''/E') values recorded in a temperature range from 25 °C to 120 °C degrees. Figures 3.6 -3.18 give the plots of dynamic mechanical data of cured emulsions and sols.

The DMTA curves show that in the case of paraffin and PEG filled samples increasing filler content decreases the T_g . In samples filled with Wood's metal which has a modulus much higher than both paraffin and PEG there is slight changes in the T_g with increasing filler content (Figure 3.15).

For Wood's metal filled samples with up to 40 per cent filler there is no apparent decrease in storage modulus (E') at the melting point of the filler. At the filler concentration above 50 per cent, however, there is dramatic decreases in storage modulus around 68 °C, the melting of the filler. Storage modulus of a filled sample correlates well with volume fraction of the filler. The density of Wood's metal is 9.67 g/cm³ and the weight percentages translate to very low volume fractions. For example, a 30 per cent (w/w) correlates to 5 per cent (v/v). At these low volume fractions the material is insensitive to the phase change of the filler. However, after 60 per cent the volume fraction becomes more than 15 per cent (v/v) and the effect of the phase change of the filler becomes measurable. In these samples we demonstrated that the Wood's metal is load bearing and that mechanical properties show a dramatic change at the melting point of the filler.

Table 3.2. Maximum working temperatures of some metal filled samples

| Wood's metal percentage | Maximum working temperature (°C) |
|-------------------------|----------------------------------|
| 0 | 75 |
| 5 | 72 |
| 20 | 73 |
| 60 | 63 |
| 70 | 53 |

Maximum working temperature is defined as the temperature at which a material shows 10 per cent loss of its modulus at room temperature. It is a measure of the highest

working temperature of a given material. DMTA curves can give an idea of maximum working temperature. The maximum working temperature data for the filled samples is given in Tables 3.2 3.3 and 3.4. For Wood's metal filled samples, no change is observed in maximum working temperature up to 60 per cent (w/w) (15 per cent v/v) filler content. Above this value there is a sharp decrease in maximum working temperature.

PEG and paraffin filled samples show dramatic changes in maximum working temperature as the filler concentration changes. For paraffin filler, concentration as low as 5 per cent leads to a reduction of maximum working temperature from 75 °C to 46 °C. It is possible that the partial solubility of sodium stearate, surface active agent used in UPE, may have an effect on the matrix mechanical properties, and the reduction in maximum working temperature is due to the matrix as well as the phase change of the filler.

Table 3.3. Maximum working temperature of paraffin filled samples

| Paraffin percentage | Maximum working temperature (°C) |
|---------------------|----------------------------------|
| 0 | 75 |
| 5 | 46 |
| 10 | 41 |
| 20 | 43 |

For paraffin filled polyester samples, decrease of storage modulus is observed with increasing paraffin amount as shown in Figure 3.10 and 3.11. Even at 5 per cent paraffin, room temperature modulus of sample is lower than that of polyester. Modulus of the sample is also lower than pure polyester at the maximum working temperature. Unlike metal filled samples, paraffin filled samples show a clear relationship between percentages and changes. Relatively small increase in the amount of paraffin causes very observable changes in E' , E'' , and $\tan \delta$ values. Dynamic moduli of samples containing different percentage of paraffin are shown in Figure 3.10 Modulus decreases very fast. From 5 per cent to 10 per cent filled samples, there are small changes and at 20 per cent a large change is observed. Also, maximum working temperature of samples decreased with increasing amount of paraffin. Moreover, E'' curves are getting broad with increasing amount of paraffin (Figure 3.13).

The density of paraffin (0.8 g/cm^3) is close to the density of UPE ($1.1- 1.2 \text{ g/cm}^3$) so the weight ratio of paraffin is nearly the same with the volume ratio. Thus, mechanical changes correlate well with weight fraction of paraffin in the sample.

Table 3.4. Maximum working temperature of some PEG filled samples

| PEG-4000 percentage | Maximum working temperature ($^{\circ}\text{C}$) |
|---------------------|--|
| 0 | 75 |
| 5 | 68 |
| 10 | 59 |

For PEG-4000 filled polyesters, an increase in PEG amount results in decrease at E' , and $\tan \delta$ values. E'' peaks are getting broad with the increasing amount of PEG. Besides these, the maxima of $\tan \delta$ curves shifted to the lower temperatures as the amount of filler increase in samples. Plasticized polymers, also, shows the similar behavior. Thus, we can conclude that some amount of PEG penetrated to polyester matrix and acted as a plasticizer (Figure 3.18) and the mechanical property changes are due to both the matrix and the filler.

For paraffin and Wood's metal samples storage modulus (E') decreases around the melting point of the filler which shows that the filler is bearing load in the sample. This observation leads us to believe that with further work, intelligent materials that show a dramatic change in modulus at a desired temperature can be manufactured by using phase changeable fillers.

In summary, we observed a regular decrease in maximum working temperature with increased filler content and a reduction in the modulus around the temperature of phase change of the filler in most of our samples.

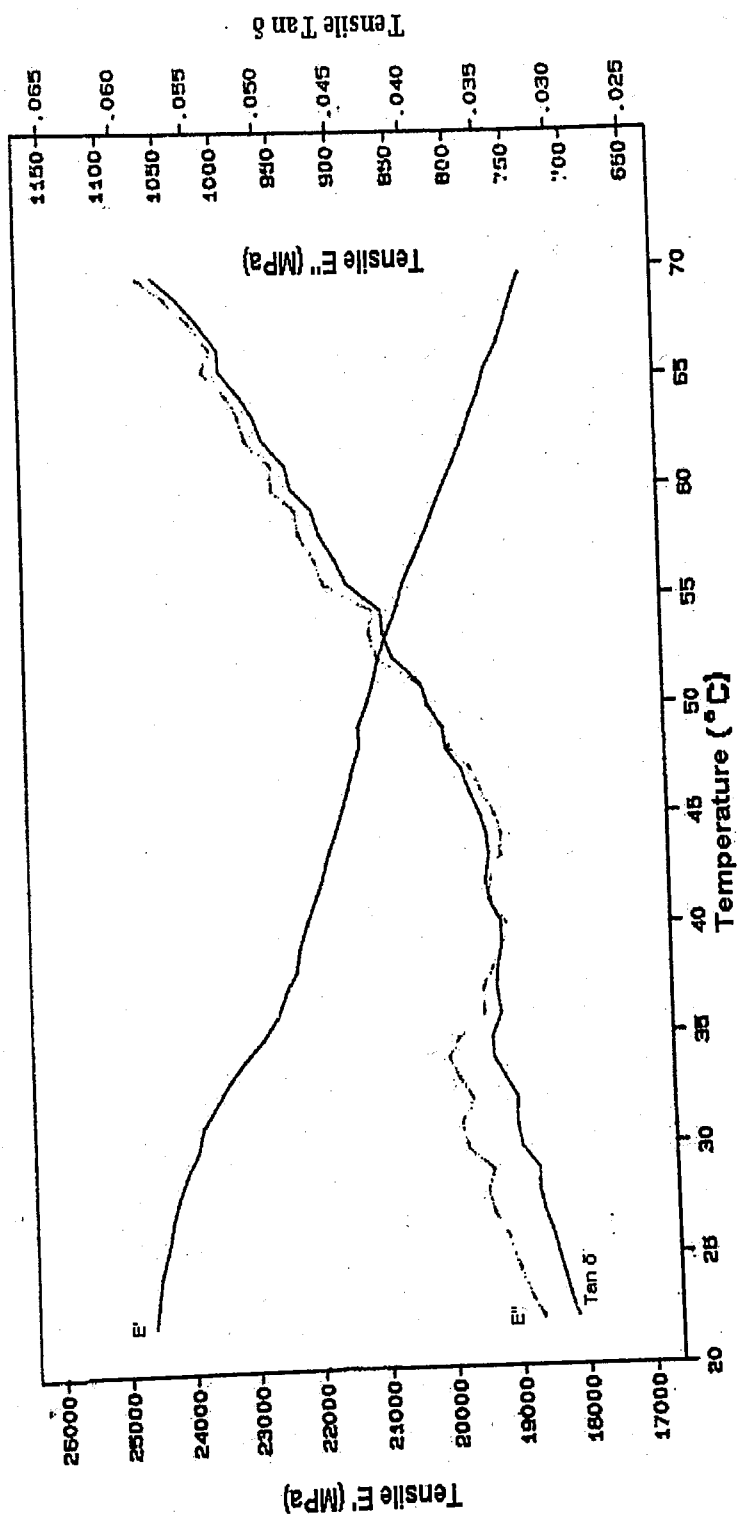


Figure 3.6. DMTA graph of Wood's metal

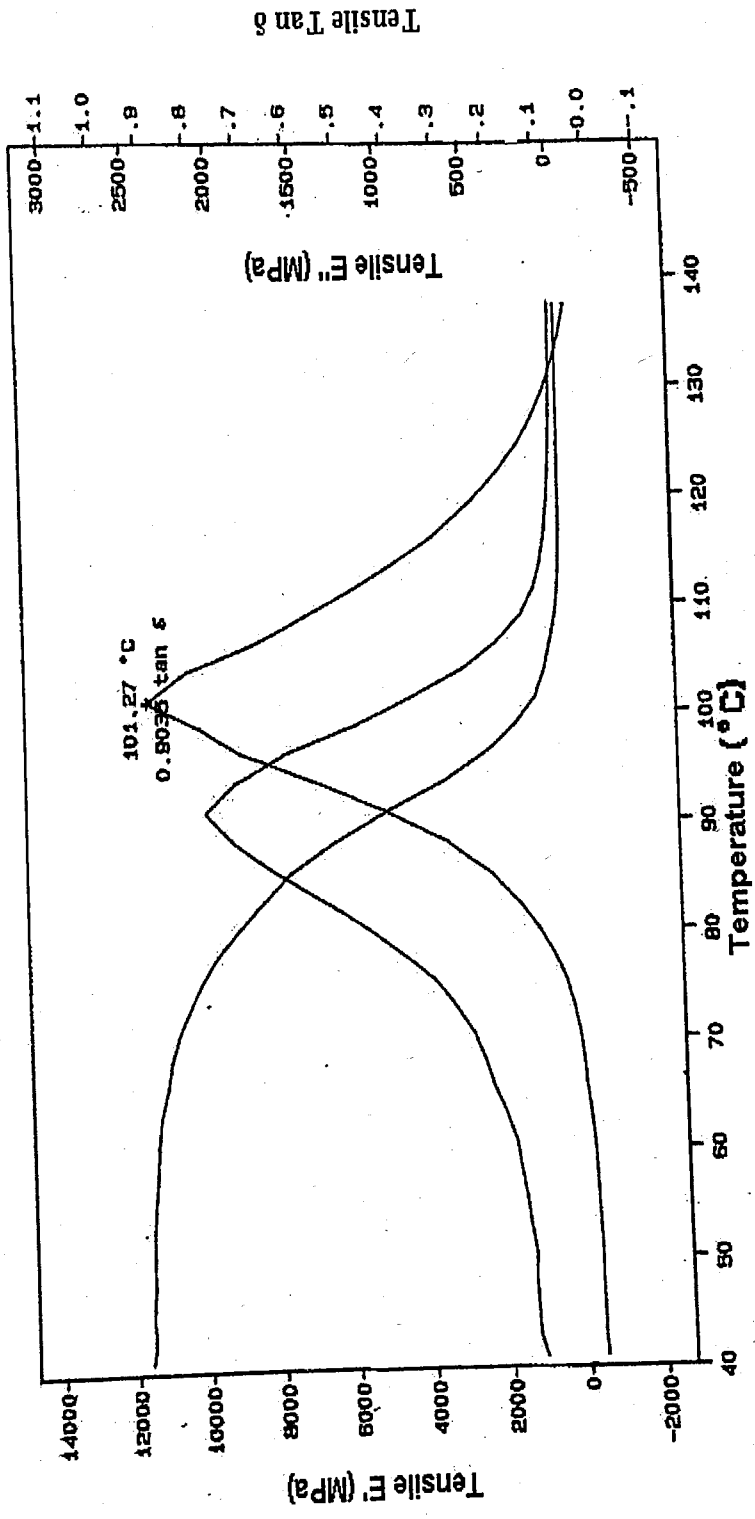


Figure 3.7. DMTA graph of cured polyester

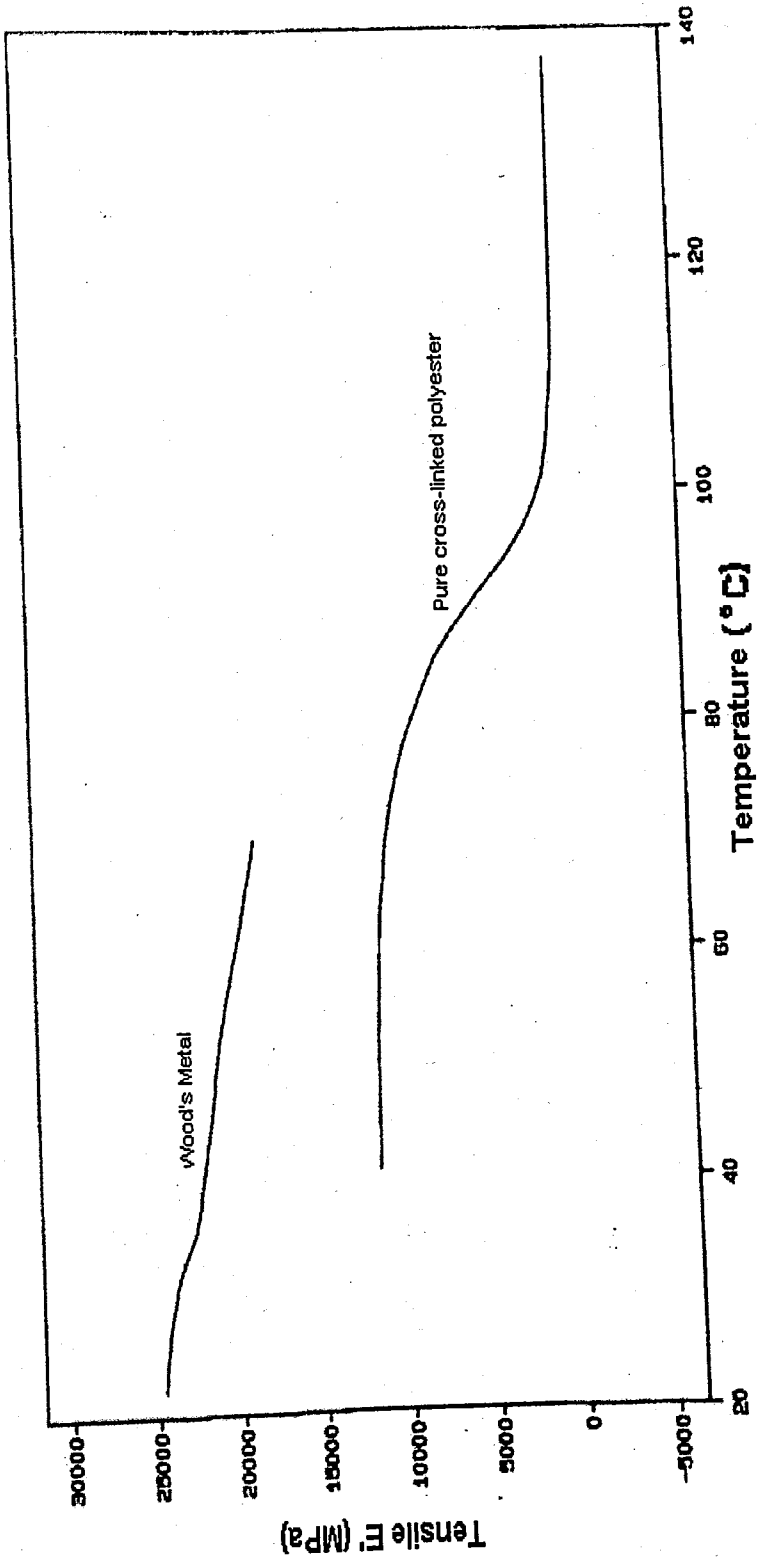


Figure 3.8. E' curves of wood's metal and neat polyester

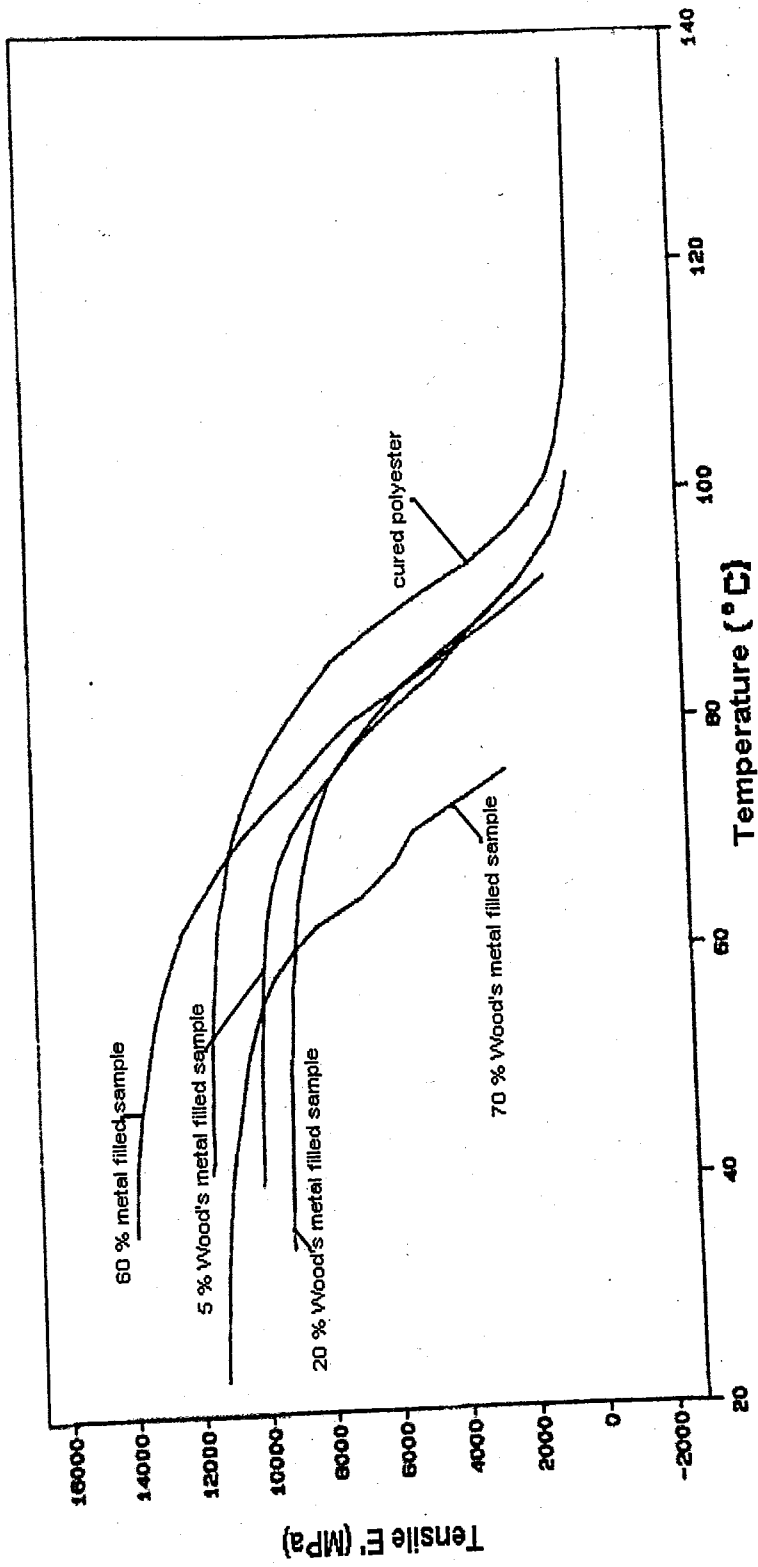


Figure 3.9. E' curves of Wood's metal filled polyester samples

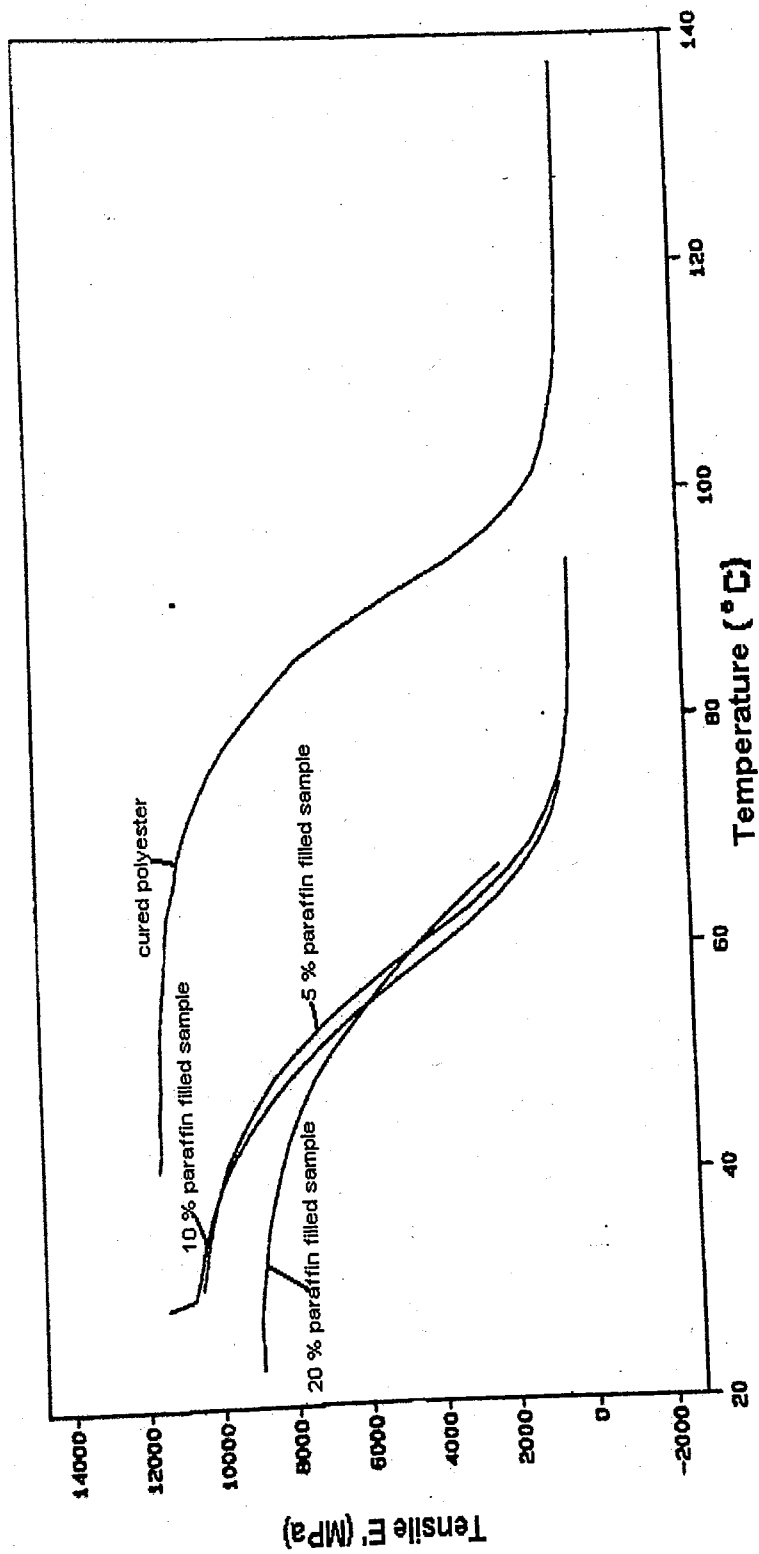


Figure 3.10 E' curves of paraffin filled polyester samples

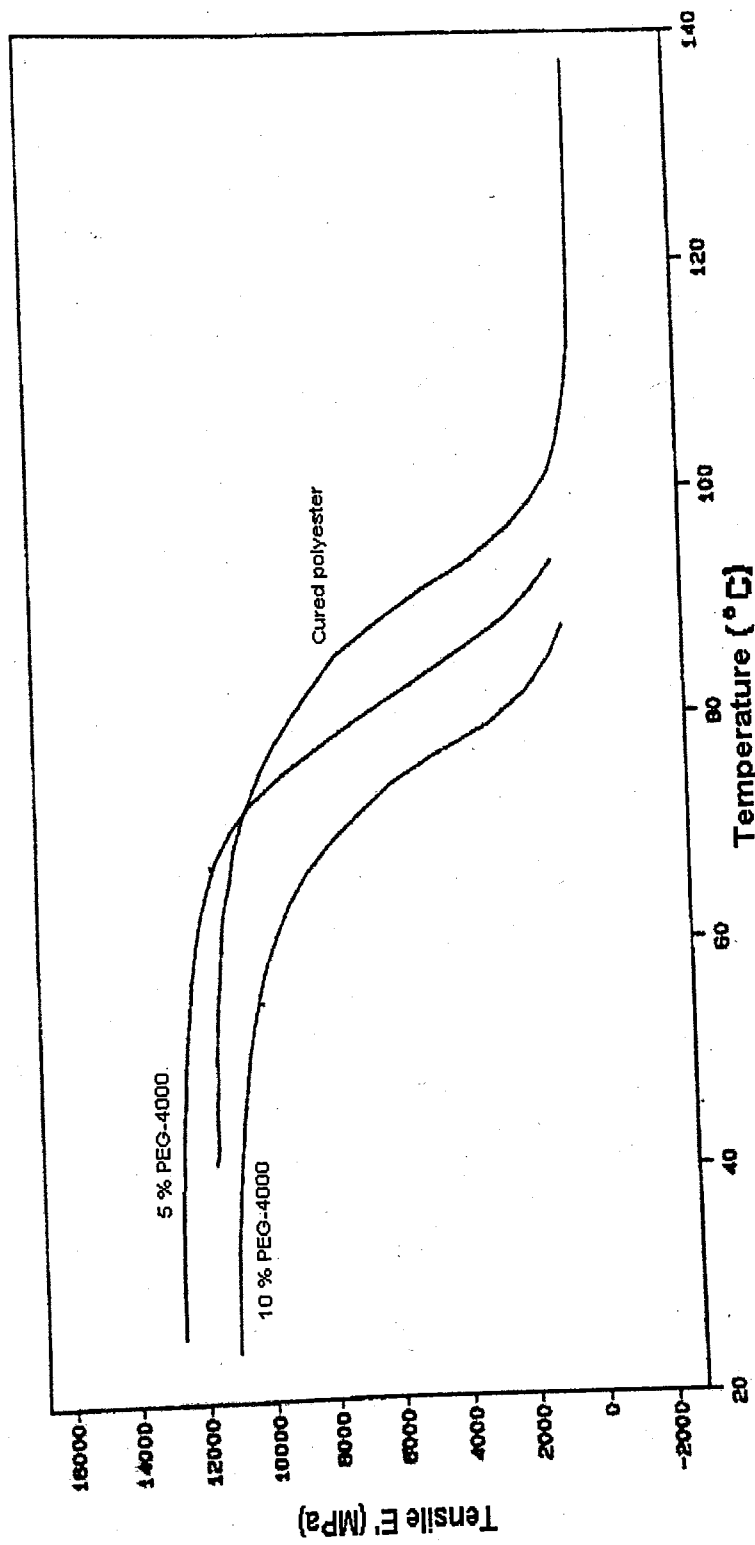


Figure 3.11. E' curves of PEG-4000 filled polyester samples

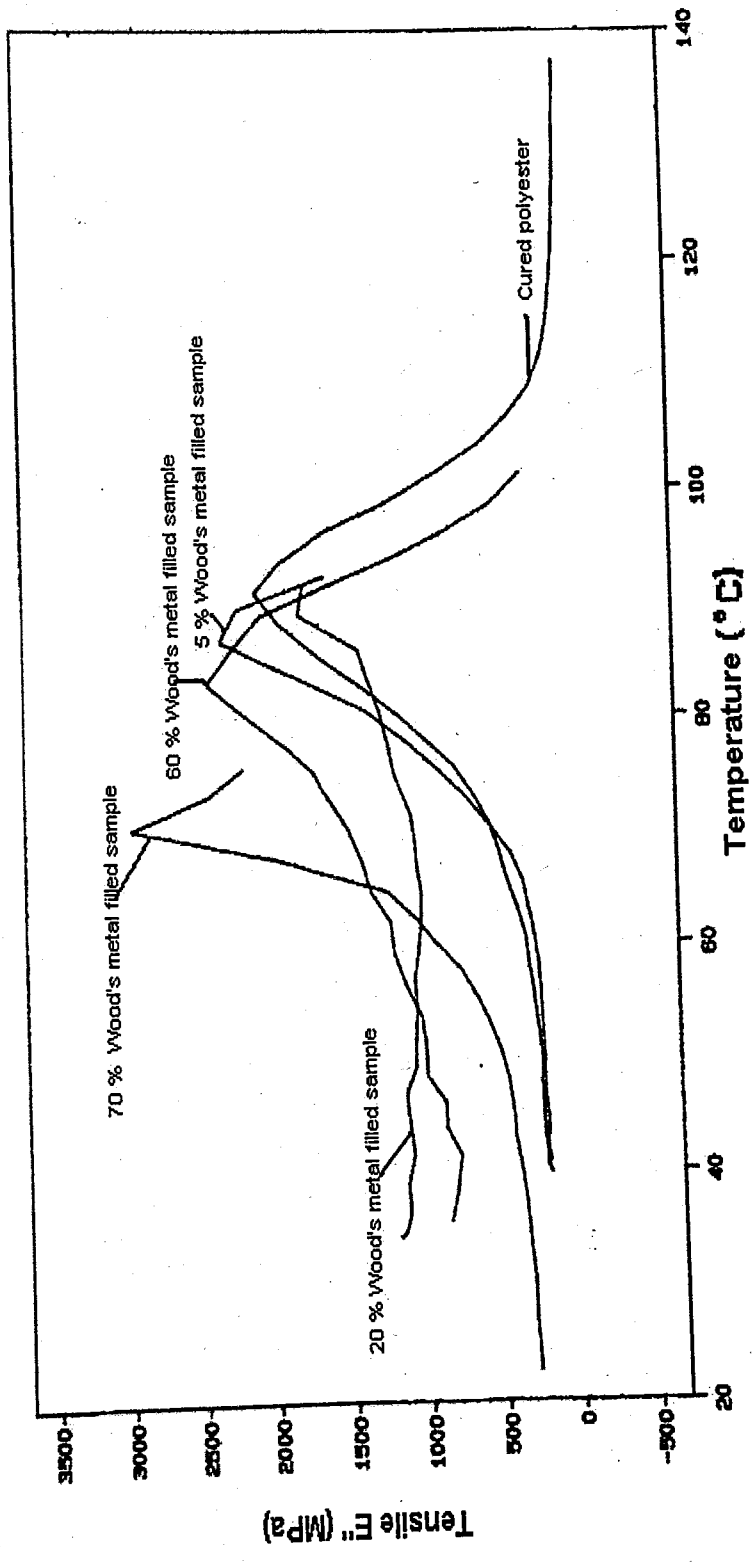


Figure 3.12. E'' curves of Wood's metal filled polyester samples

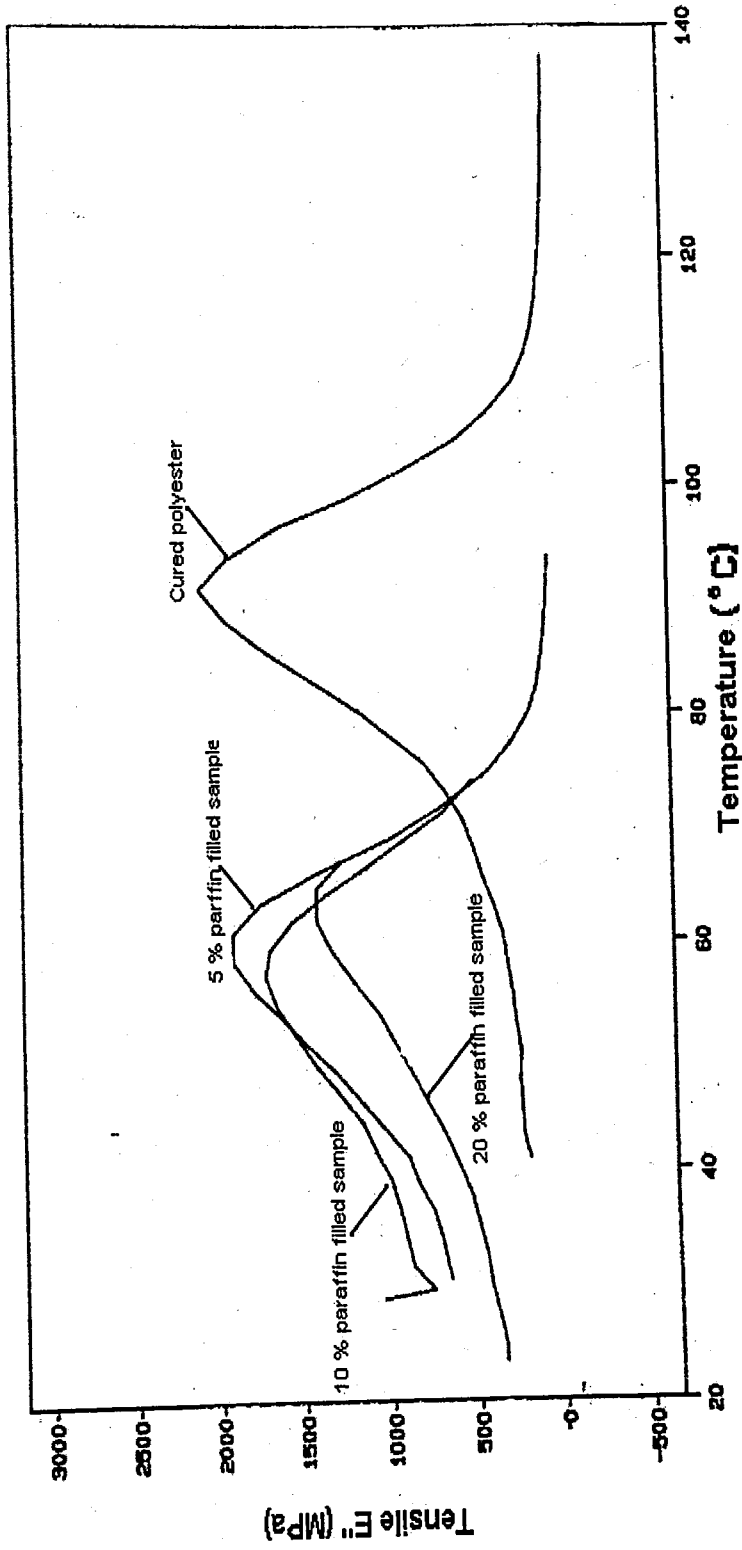


Figure 3.13. E'' curves of paraffin filled polyester samples

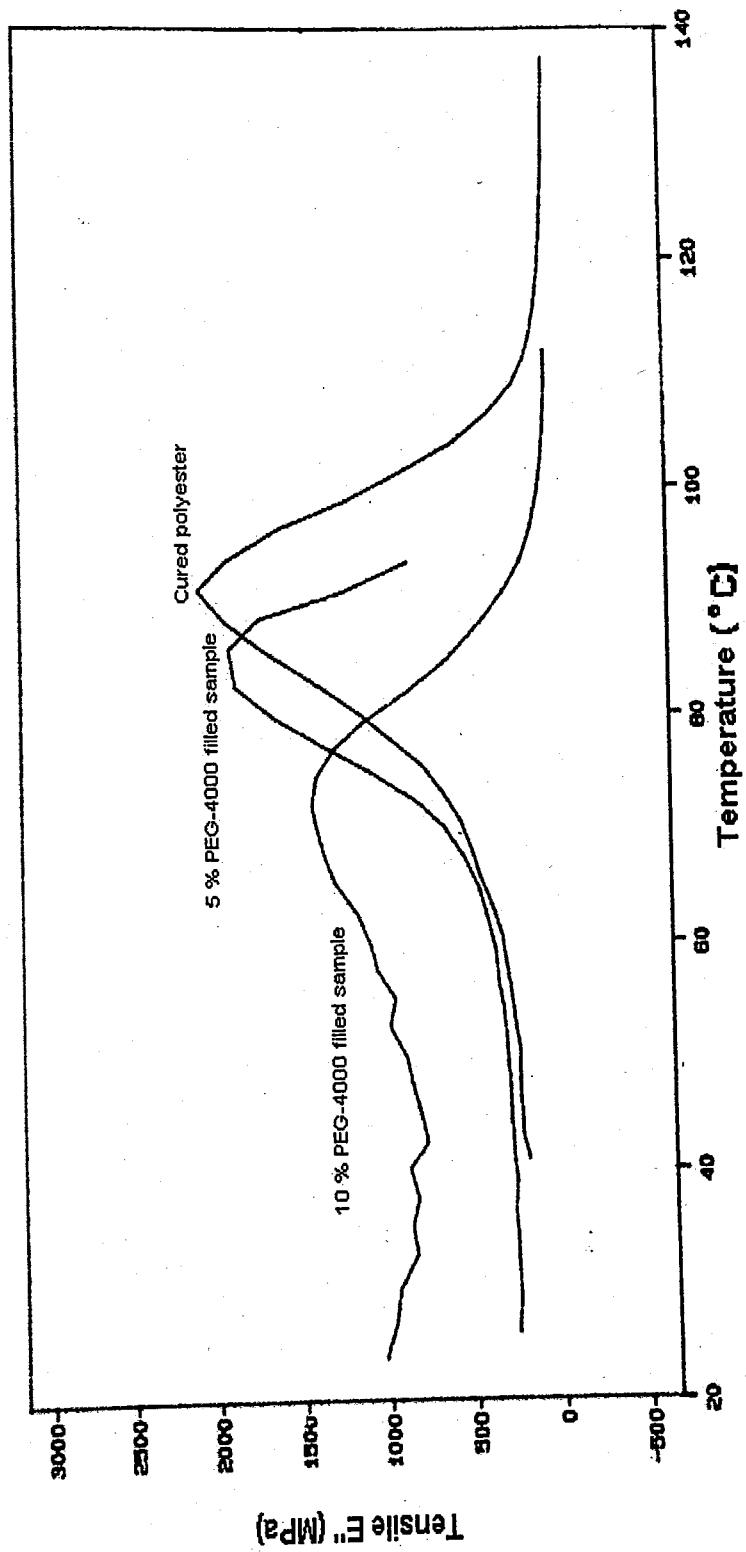


Figure 3.14. E'' curves of PEG-4000 filled polyester samples

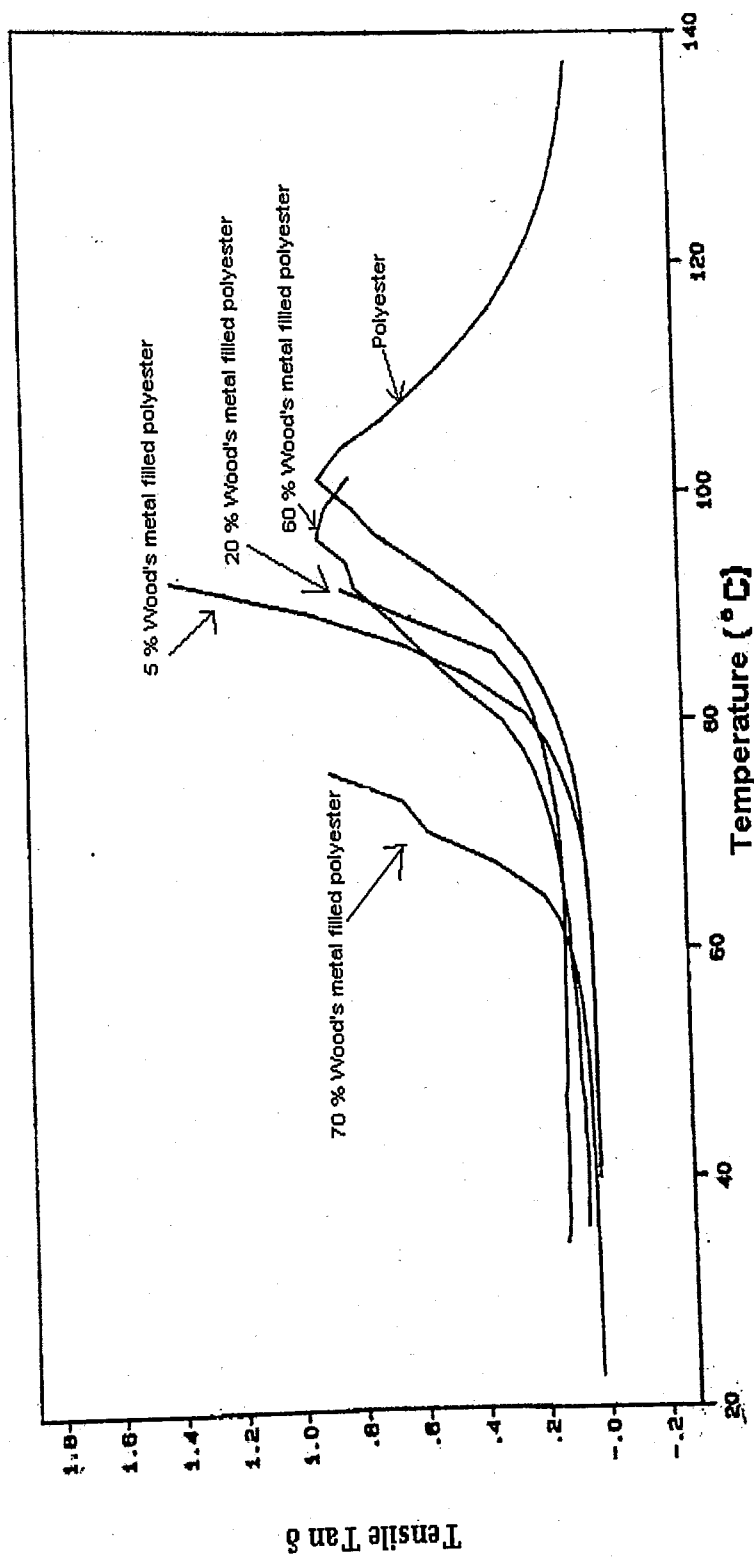


Figure 3.15. Tan δ curves of Wood's metal filled polyester samples

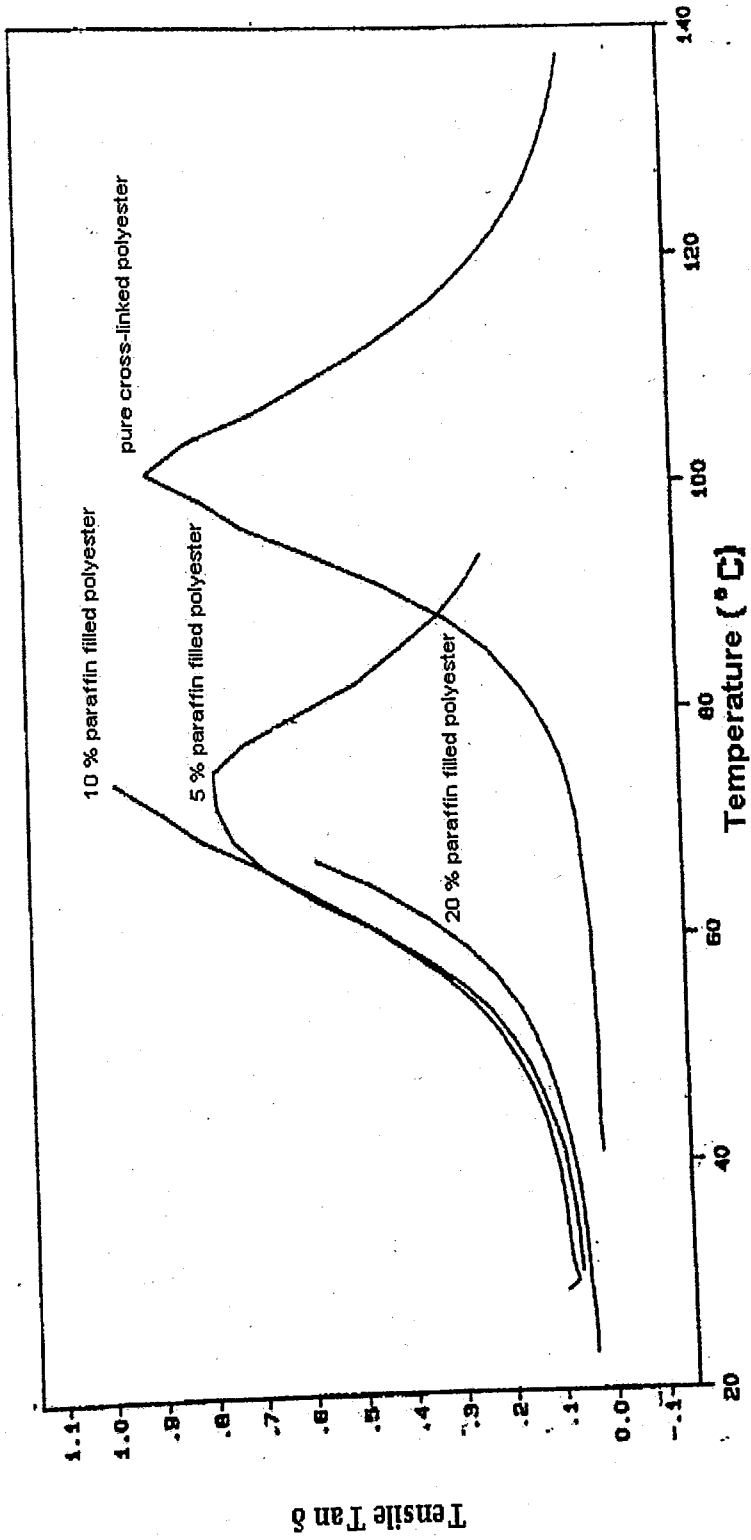


Figure 3.16. Tan δ curves of paraffin filled polyester samples

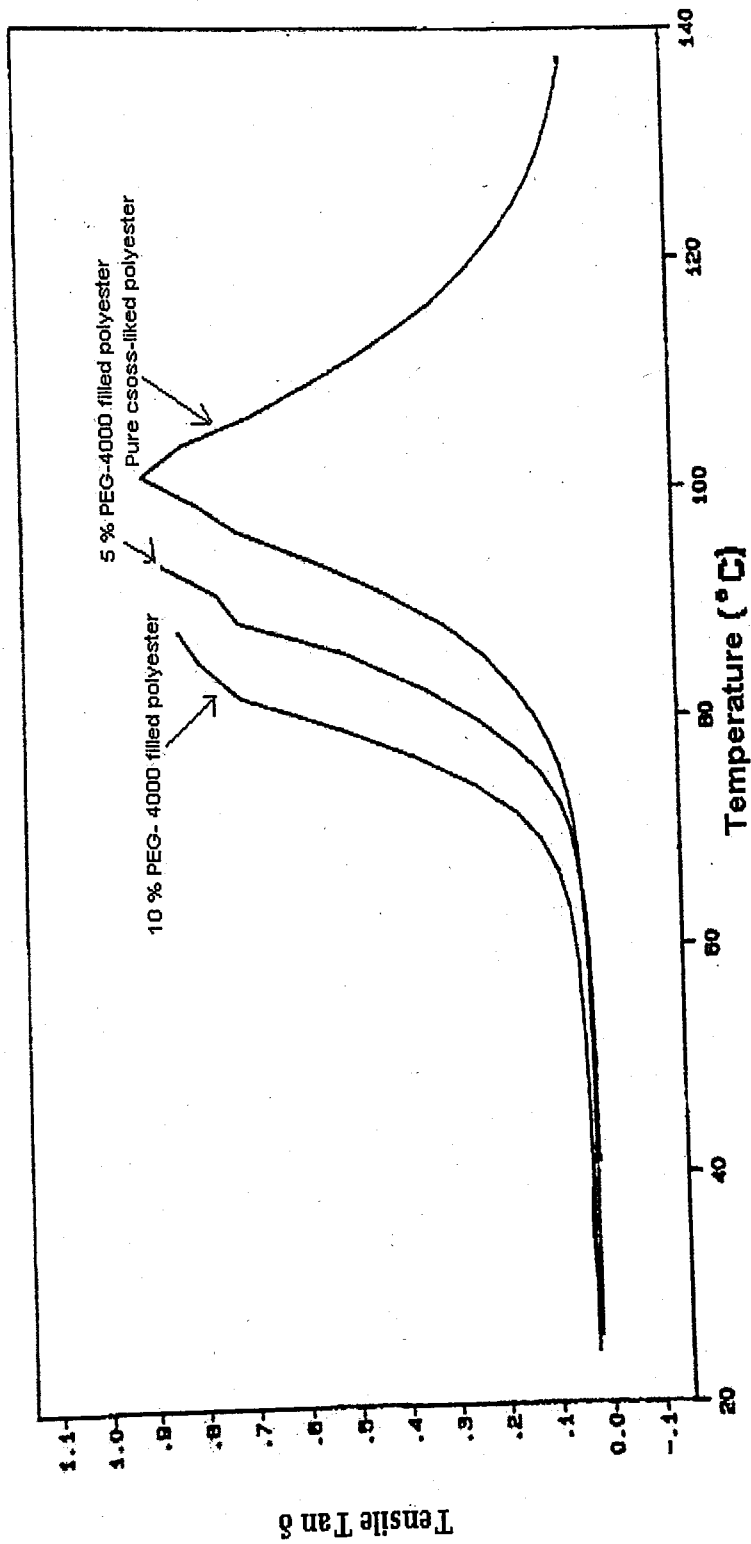


Figure 3.17. Tan δ curves of PEG-4000 filled polyester samples

3.2.2. DSC Analysis

DSC is the most versatile instrument for the measurements of energy changes in material. Hence, it is most applicable of all thermal analysis methods.

In this study, we prepared polyester samples that include PCMs. One of the most important characteristics of PCMs is that they show energy absorption at the melting point. PEG-4000, Paraffin, and Wood's metal filled polyester samples were tested by DSC from 25°C to 120°C. Melting behavior should be observed around melting point of filler since at these temperatures fillers change their phase and they absorb heat. This reversible process causes an endotherm, which indicates a melting phenomenon, in the DSC graph (Figure 3.18). The DSC graphs of pure PEG-4000, paraffin, and Wood's metal are shown in Figures 3.20 3.21 and 3.22. PEG-4000 has the maximum heat of fusion (Figure 3.21) and paraffin has the second highest heat of fusion (Figure 3.22).

Pure cross-linked polyester did not exhibit any melting transition, as shown in Figure 3.19. Therefore, melting transitions of any filler in the cross-linked polymer matrix should be easily determined

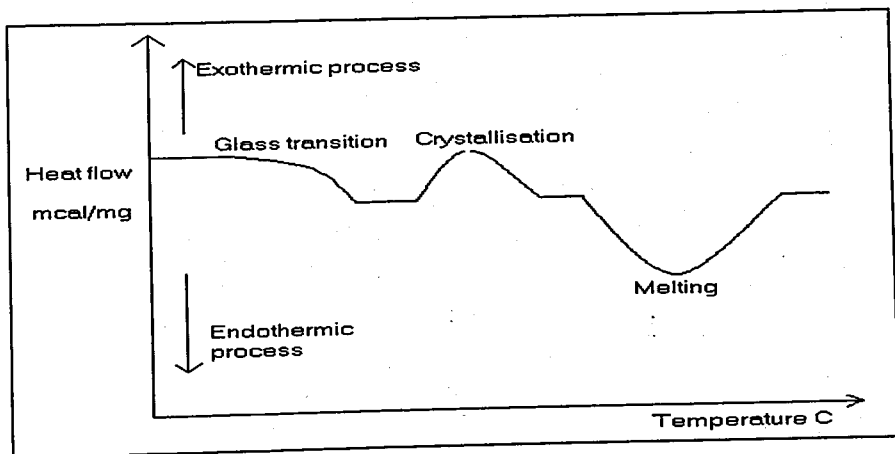


Figure.3.18. General DSC graph

Although Woods metal shows a good melting transition (Figure 3.20), its weight specific heat of fusion is relatively small because of the high density of metal.

Melting transitions in samples filled with paraffin and woods metal can be observed in DSC graphs (Figures 3.25 3.26 and 3.27). However, samples prepared with PEG-4000 did not exhibit any transition (Figures 3.23 and 3.24). This indicates that there is no solid crystalline PEG-4000 in the polyester matrix. PEG-4000 filled samples were prepared by mixing saturated PEG-4000 aqueous solution in polyester followed by cure. So the emulsions in the matrix contain a PEG-4000 - water solution which is a liquid at room temperature and does not show a phase change when heated.

On the other hand, polyester samples with paraffin and wood's metal exhibited well defined melting transitions in DSC graphs. The area of melting transitions increases as the amount of filler increase. The melting transitions of paraffin and Wood' metal filled polyester samples are shown in Figures 3.25 and 3.26, respectively. Melting transition was completed in a narrow temperature range, 69 °C to 74 °C, in Wood's metal filled samples. However, the melting transition of paraffin filled samples was completed in broader temperature range than Wood's metal filled samples which indicates that paraffin includes different crystalline regions of different molecular weight aliphatic carbon chains. Melting transitions started at 40 °C in DSC spectra which was verified by the start of modulus loss in the DMTA spectra.

This behavior of our samples is new and unique. At the melting point of the filler, material shows an endotherm but it does not melt. To our knowledge, there is no such material produced or described before. With the correct choice of the filler, materials that absorb or emit heat at chosen temperature without physically melting can be produced. Materials that can absorb and release heat reversibly but still remain as a load bearing solid during this process becomes a possibility through our work.

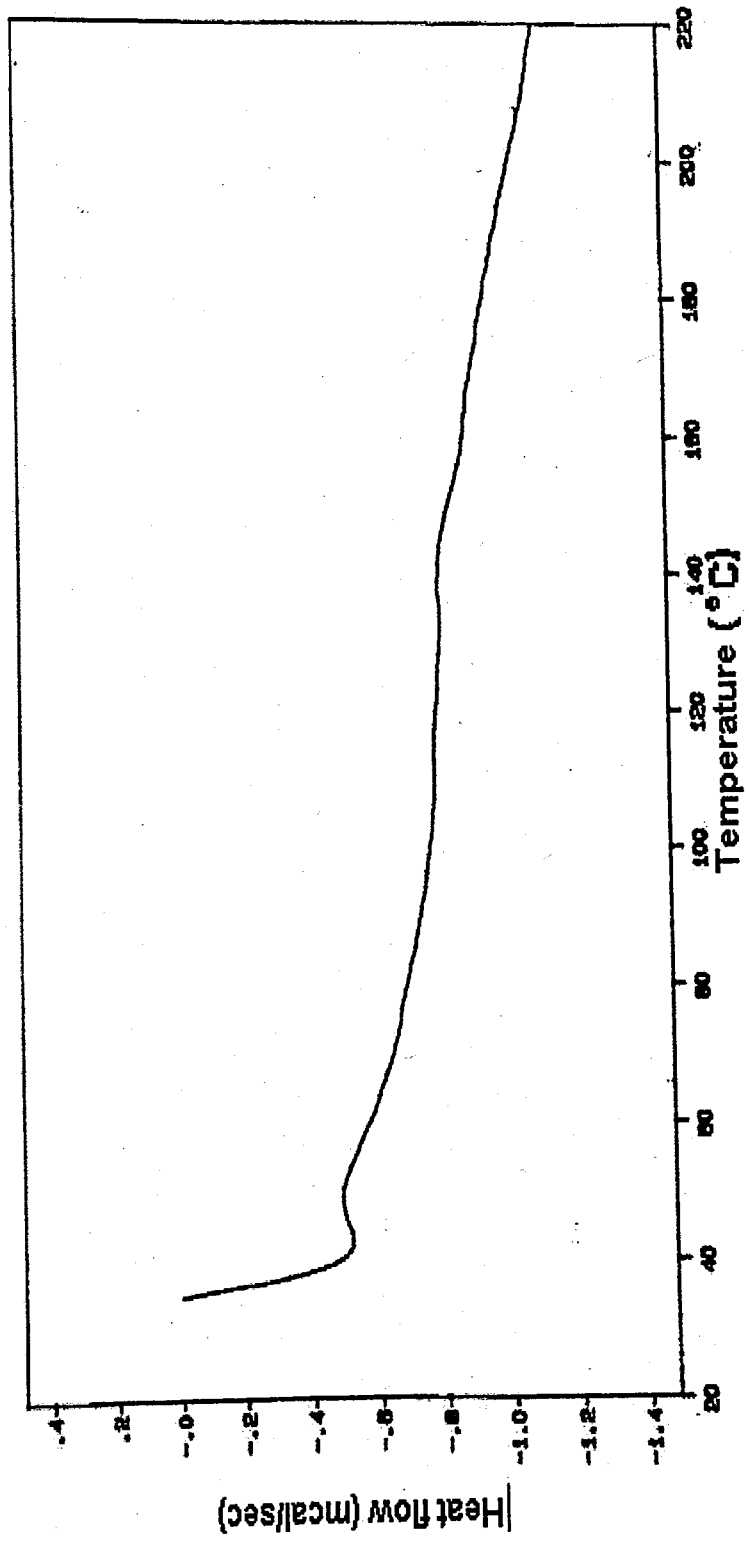


Figure 3.19. DSC curve of neat polyester

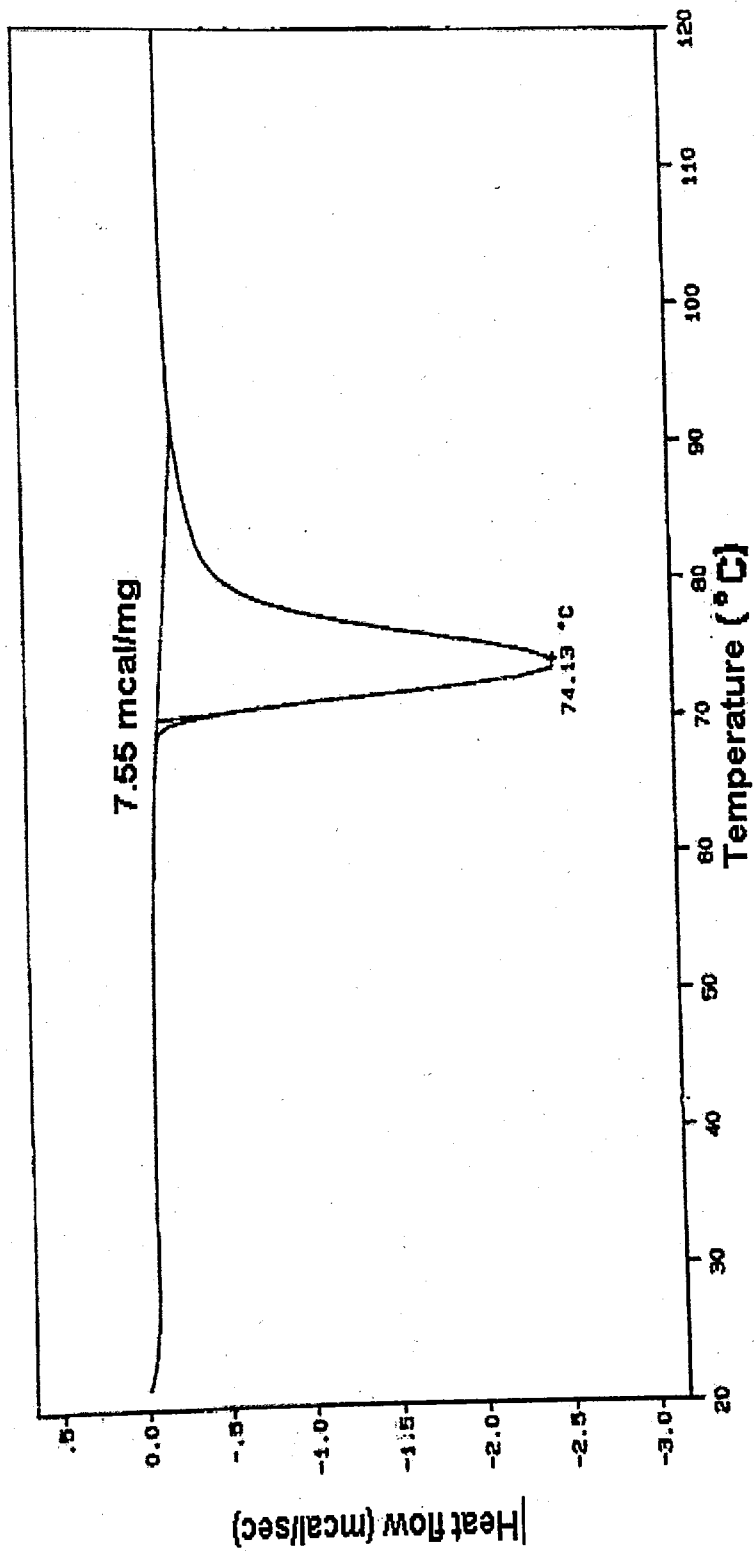


Figure 3.20. DSC curve of Wood's metal

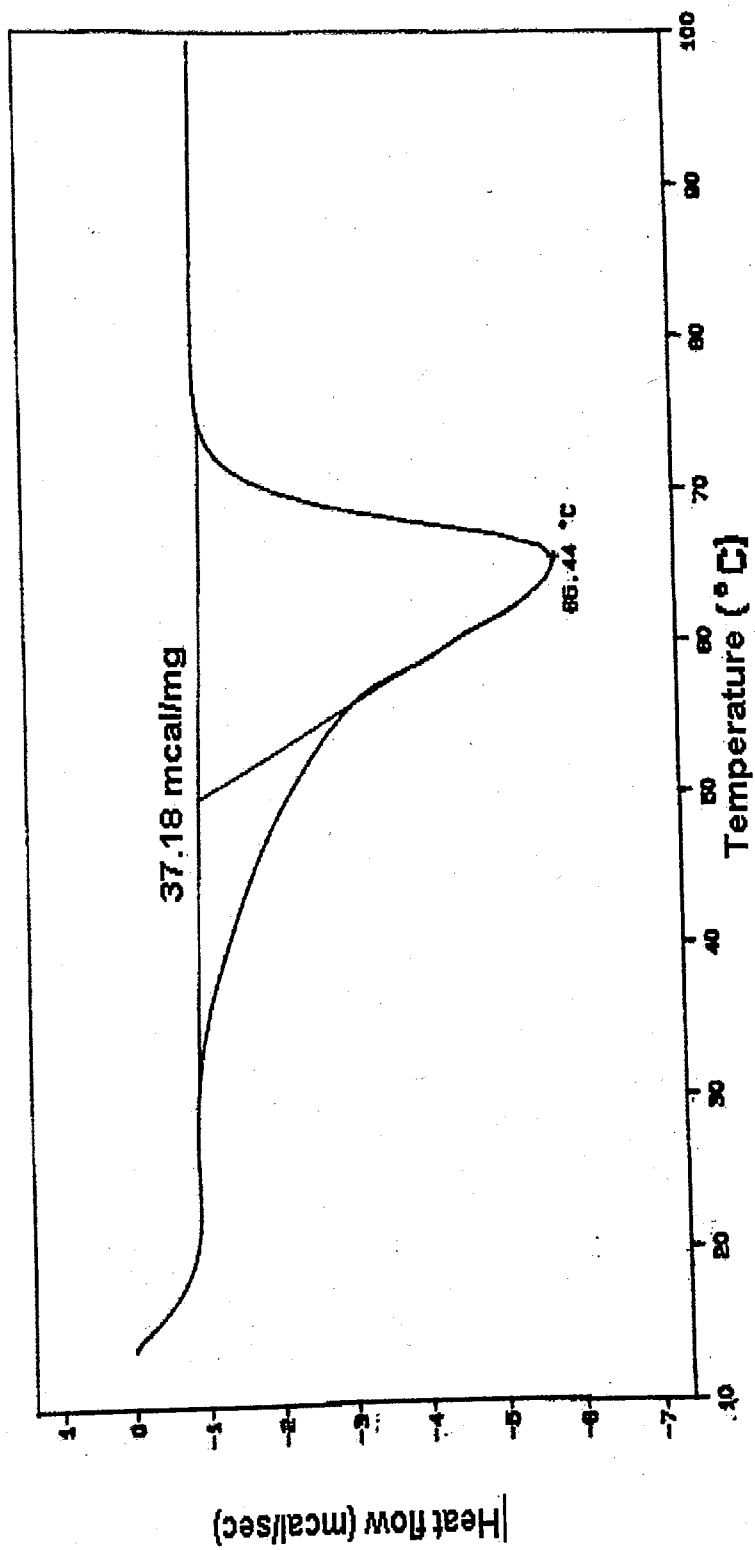


Figure 3.21. DSC curve of paraffin

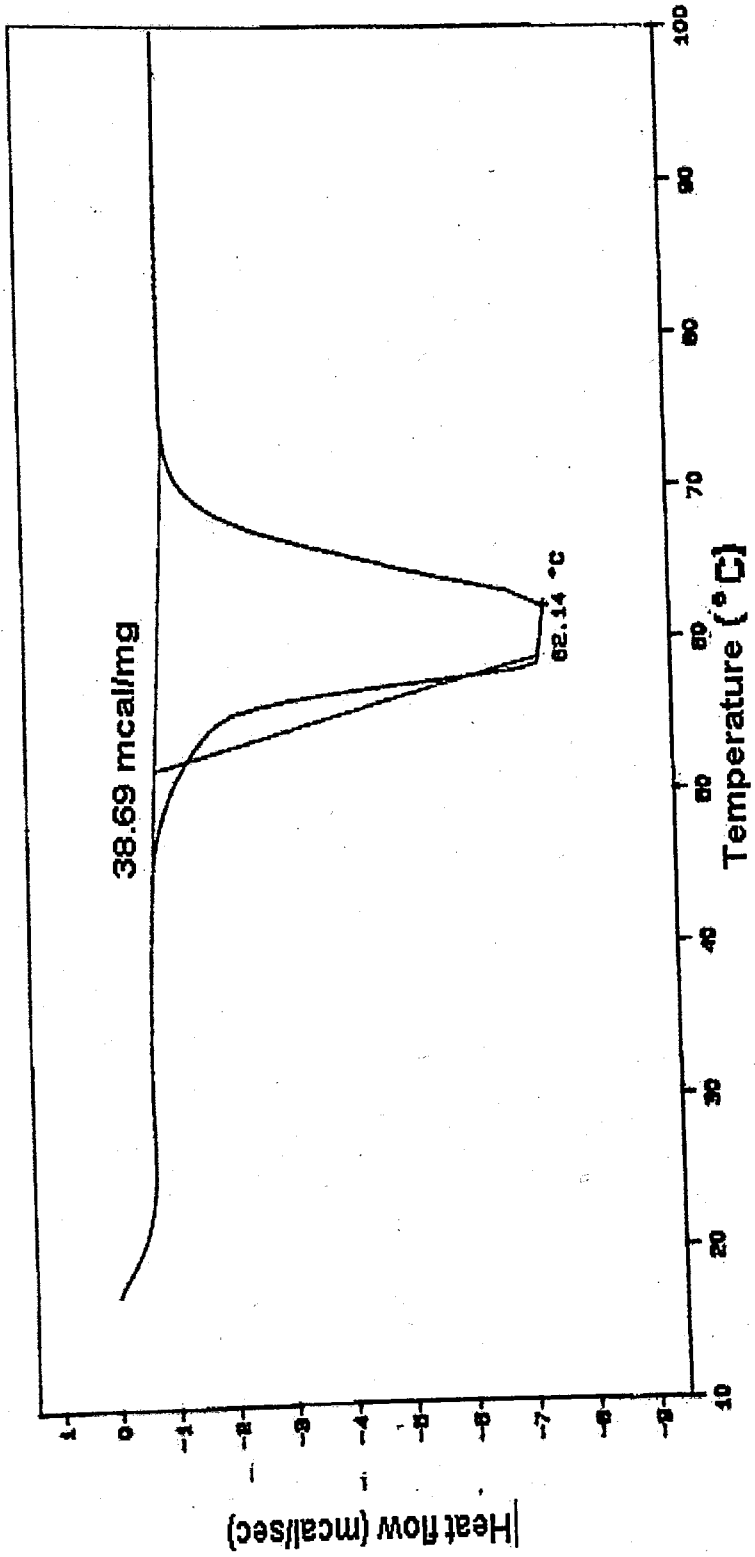


Figure 3.22. DSC curve of PEG-4000

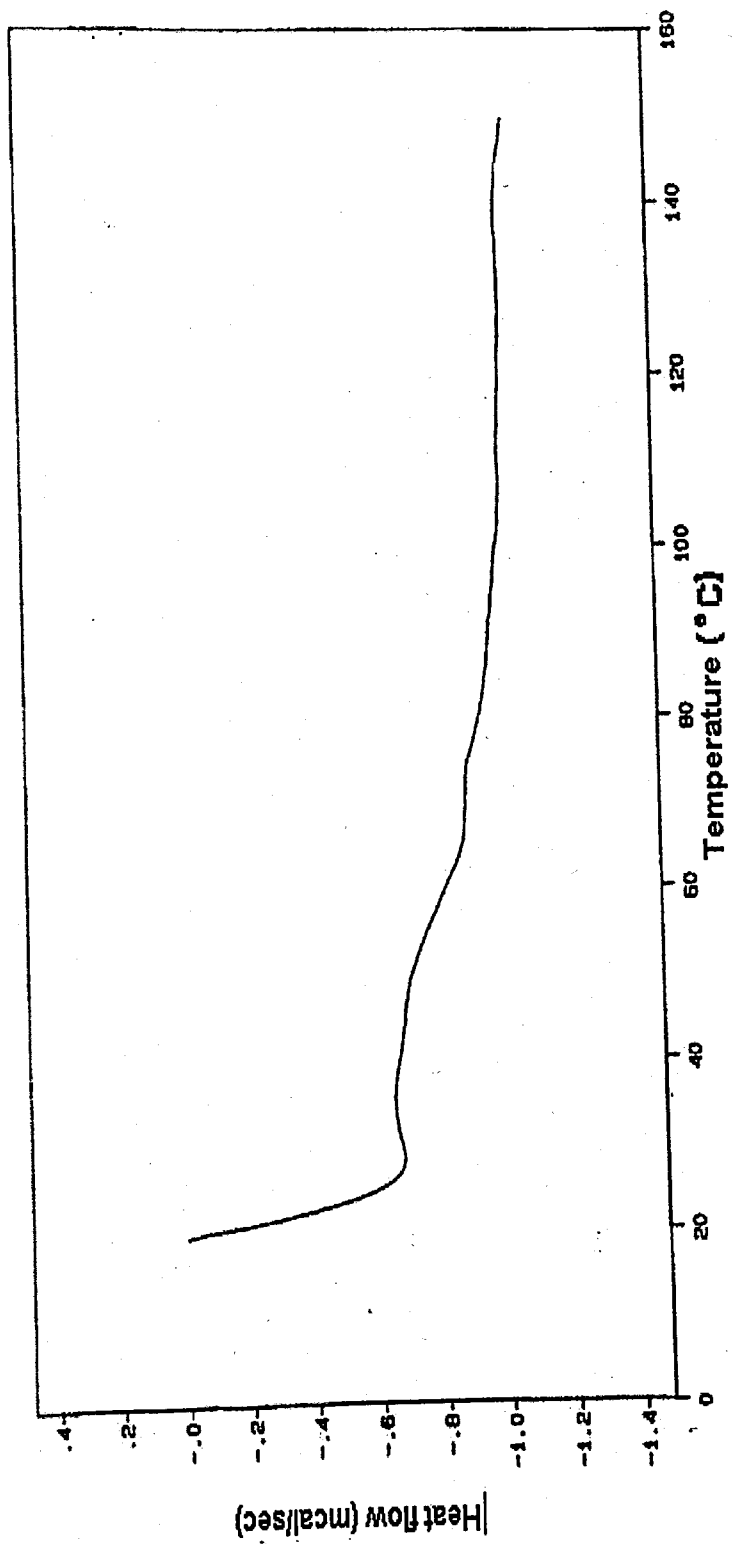


Figure 3.23. DSC curve of 5 % PEG-4000 filled polyester

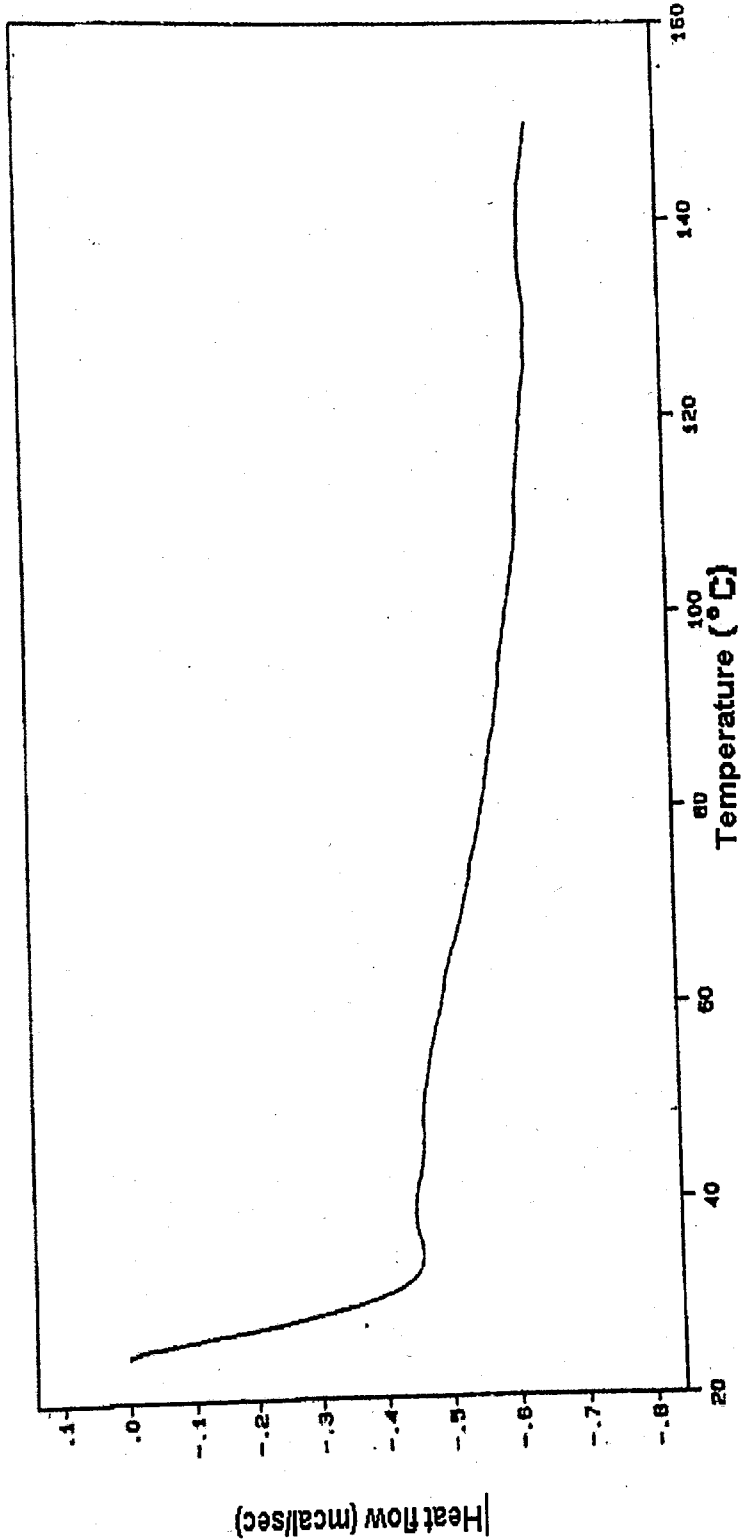


Figure 3.24. DSC curve of 10 % PEG-4000 filled polyester

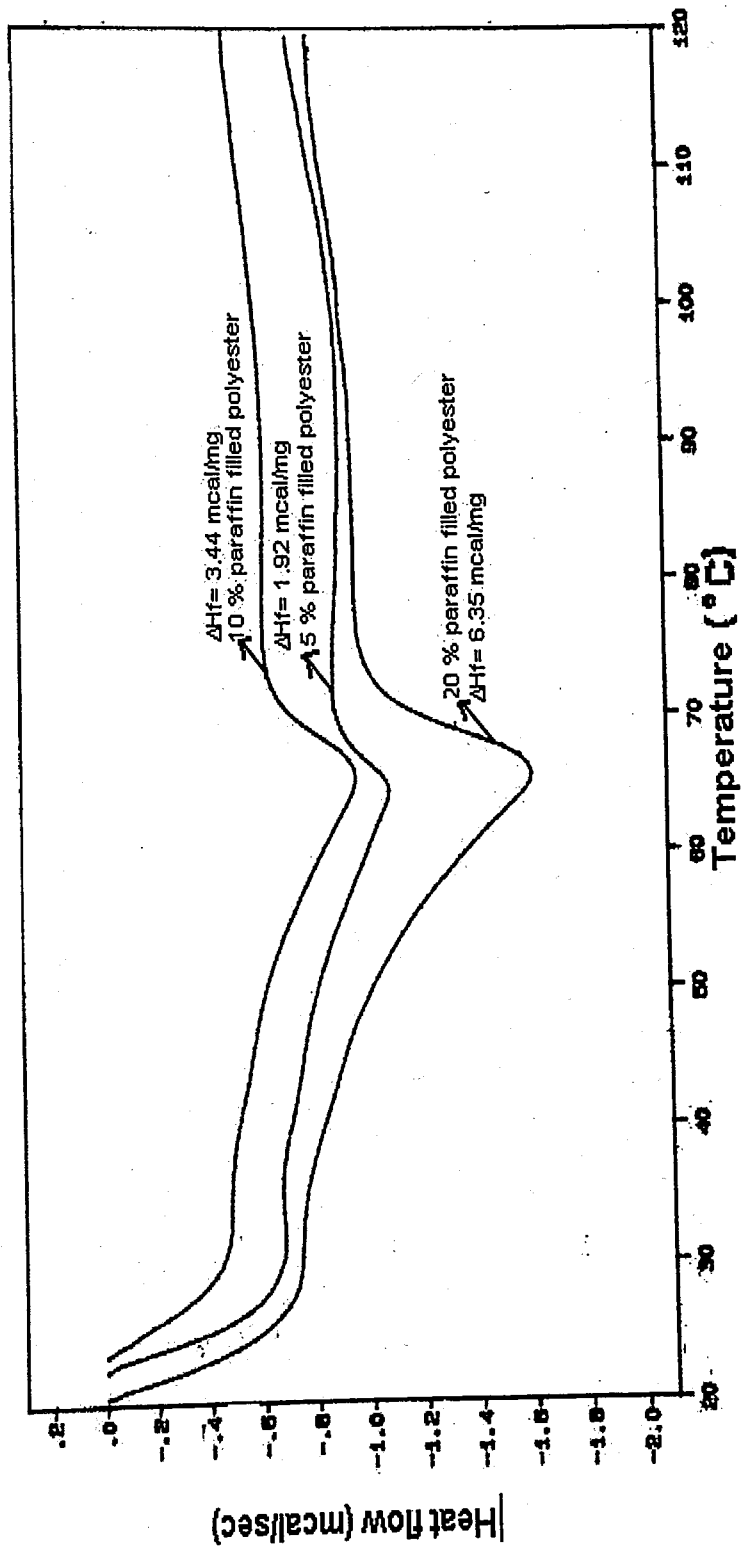


Figure 3.25. DSC curves of paraffin filled polyester samples

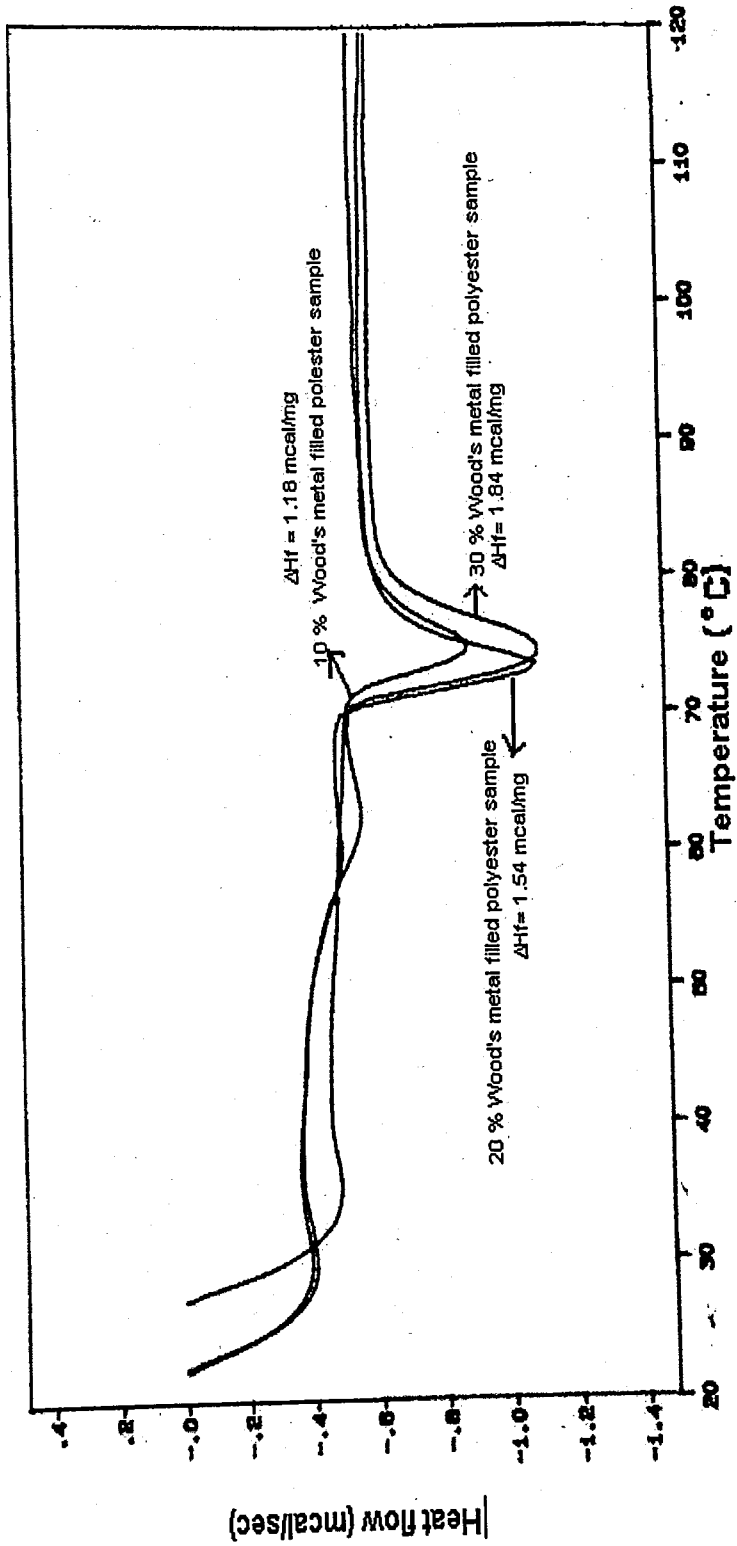


Figure 3.26. DSC curves of Wood's metal filled polyester samples

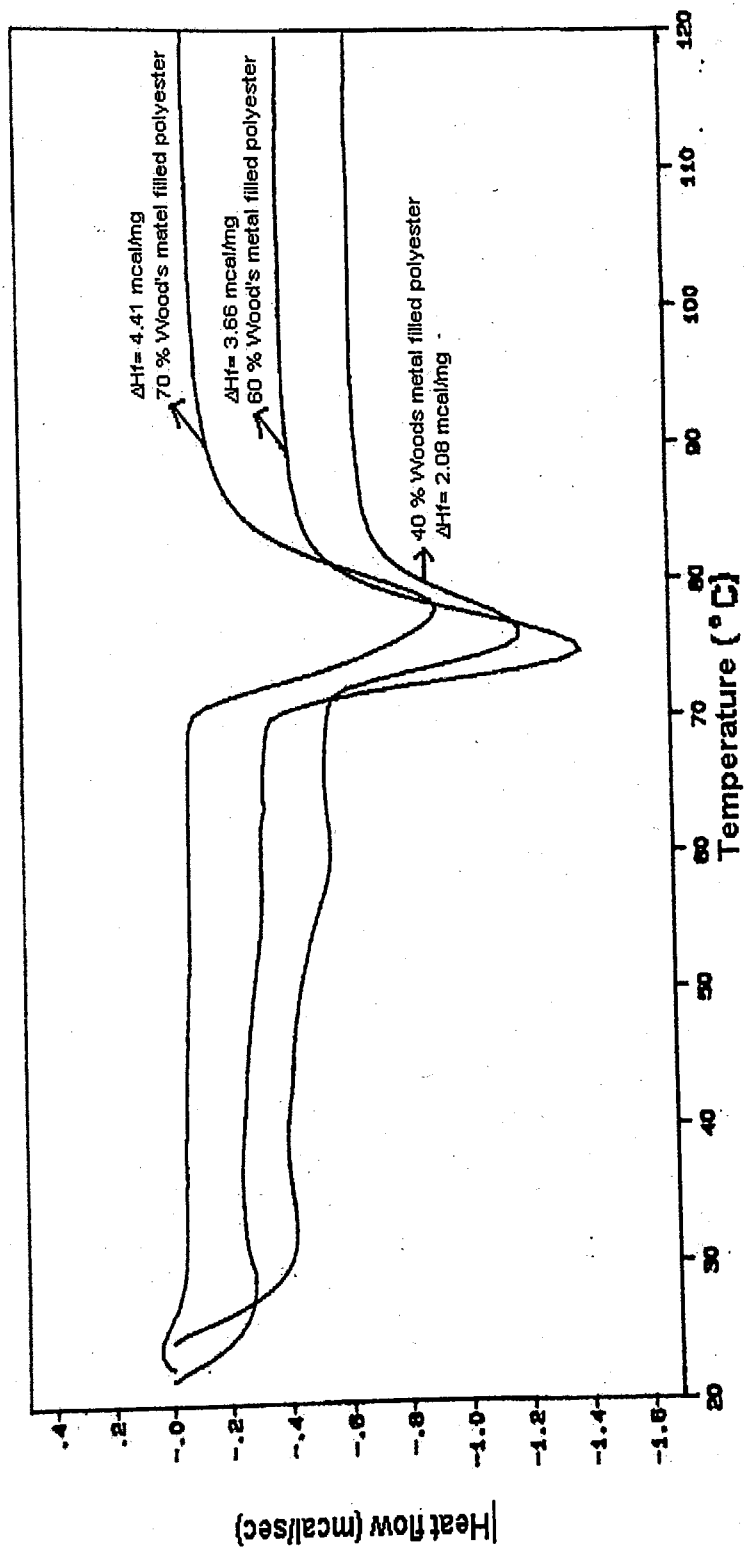


Figure 3.27. DSC curves of Wood's metal filled polyester samples

3.2.3. Surface Hardness

Hardness tests involve the quantitative assessment of the resistance to penetration of material by an indenter. The test pieces must be mechanically unstressed before the test. Standard samples have a sufficient size to allow the standardised test and a minimum thickness of three mm (Shore D).

Table 3.5. Shore hardness of Wood's metal filled polyester

| Metal percentage | Surface hardness at 21 °C | Hardness at 80 °C |
|------------------|---------------------------|-------------------|
| 0 | 86,0 | 80,6 |
| 5 | 86,8 | 75,0 |
| 10 | 87,4 | 74,6 |
| 20 | 88,5 | 77,0 |
| 30 | 88,0 | 76,3 |
| 40 | 86,8 | 75,0 |
| 60 | 81,0 | 40,0 |
| 70 | 80,5 | 35,0 |
| 80 | 34,0 | Out of scale |

Table 3.6. Shore hardness of paraffin filled polyester

| Paraffin percentage | Hardness at 22 °C | Hardness at 60 °C |
|---------------------|-------------------|-------------------|
| 0 | 86,0 | 80,6 |
| 5 | 56,0 | 16,0 |
| 10 | 53,0 | 15,0 |
| 20 | 42,0 | 13,0 |

A minimum of five tests was performed at different points on a specimen. Tests were done at room temperature (about 21 °C) and at 60°C for PEG-4000 and paraffin filled specimens and at 80°C for Wood's metal filled polyester samples. The distance between

the test points was ≥ 6 mm from each other and ≥ 12 mm from each edge of the specimen. The hardness tester was used in a vertical position and any lateral movement was avoided. The tester was applied to the specimen in a smooth manner, avoiding any shocks or vibrations until the contact shoe met the specimen. The value was read after 15 seconds after contact. The data which were obtained, is shown Tables 3.2, 3.3, and 3.4.

Table 3.7. Shore hardness of PEG-4000 filled polyester

| PEG+ Water percentage | Hardness at 22 °C | Hardness at 60 °C |
|-----------------------|-------------------|-------------------|
| 0 | 86,0 | 80,6 |
| 5 | 80,0 | 72,0 |
| 10 | 79,0 | 56,0 |
| 20 | 63,0 | 29,0 |
| 30 | 39,0 | 16,0 |

The highest hardness values were observed on the metal filled polymers. Paraffin filled polymers showed the lowest surface hardness values. These results are compatible with DMA results since metal filled polyesters show the highest E' values (Table 3.5.). As no surface active agent was used for the metal filled samples, no loss of mechanical properties was observed for the matrix. In paraffin and PEG filled samples, the surface active agents contributes some plasticization for the matrix and a reduction of surface hardness is a consequence of this plasticization.

Above the phase change temperature of the filler, dramatic decreases in the hardness were observed for samples. For Wood's metal filled samples, these increases were observed only at high metal percentage because of the high density of Wood's metal.

3.2.3.1 Significance of Hardness Tests. Hardness is not reliable measure of stiffness.

Hardness measurements derive from small deformations at the surface, whereas stiffness measurements, such as measurement of tensile modulus, derive from large deformations of entire mass.

Unlike with metals, there is no correlation between hardness and tensile strength of plastic materials. As the hardness increases, the tensile strength of material may increase to a maximum, and then decrease or it may decrease from the beginning, depending on the formulation of the compound [12].

Table 3.8. Volume per cent and Weight per cent effects of shore hardness of Wood's metal

| Weight per cent | Volume per cent | Surface hardness at 22°C | Surface hardness at 80°C |
|-----------------|-----------------|--------------------------|--------------------------|
| 5 | 0,60 | 86,8 | 75,0 |
| 10 | 1,36 | 87,4 | 74,6 |
| 20 | 3,00 | 88,5 | 77,0 |
| 30 | 5,00 | 88,0 | 76,3 |
| 40 | 7,66 | 86,8 | 75,0 |
| 60 | 16,4 | 81,0 | 40,0 |
| 70 | 22,5 | 80,5 | 35,0 |
| 80 | 33,3 | 34,0 | Out of scale |

3.2.4. SEM Analysis

SEM (Scanning Electron Microscope) is the best scientific instrument observing heterogenous polymers. By the help of this instrument, the surface features, texture, shape, size and the relative amounts of the fillers are easily detected. Magnification is from 100 to 3700.

SEM images of fractured surfaces of PEG-4000, paraffin, and Wood's metal filled polyester were obtained. The edge of PEG filled sample can be seen in Figure 3.28 which is magnified about 450 times. Some voids that are uniformly and homogenously scattered in polyester matrix can be easily seen. As the electron microscope operates 10^{-6} bar pressure, the water-PEG mixture loses its water at these low pressures. The loss of water results of the formation of voids. PEG-4000, which has a very low vapour pressure, remains in the cavities after the evaporation of water. These voids are the proof that water

exists in the samples. PEG filled material, magnified about 3700 times, is shown in Figure 3.30. In this Figure, PEG particles can be observed in the voids.

Table 3.9. Standart Test methods for Hardness Measurements [12]

| ISO Standards | Title | Corresponding National Standards |
|---------------|--|---|
| 868 | Plastics and ebonites- Determination of indentation hardness by means of a Durometer (Shoremeter) | ASTM D 22400 BS 2719 DIN 53505 |
| 48 | Vulcanised rubbers Determination of hardness (Hardness btw 30 and 85 IRHD) | ASTM D 1415 BS 903, part A 26 DIN 53519 |
| 14000 | Vulcanised rubbers of high hardness (85 to 100 IRHD). Determination of hardness | ASTM D 1415 BS 903, part A 26 DIN 53519 |
| 1818 | Vulcanised rubbers of low hardness (10 to 35 IRHD). Determination of hardness | ASTM 1415 BS 903, part A 26 DIN 53519 |

The crack surface of 30 per cent paraffin containing sample is shown Figure 3.31. The shape of paraffin particles is almost spherical and no agglomeration was observed. As the paraffin was emulsified in a molten state the spherical shape which minimizes surface area for a given volume is the expected shape. Every paraffin particle is independent of the other and a closed shell like structure was observed. Some voids are also observed and the surfaces of these voids are very smooth, which is an indication of no cohesion between paraffin particles and polyester matrix at the interface. Therefore, paraffin is not reinforcing filler for these samples. And in any case, the low modulus of the filler does not allow any reinforcement of the final product.

The crack surface of 30 per cent of metal filled polyester sample is shown Figure

3.32 Material is brittle and hard. The cracked surface represents a typical polyester surface. Although metal amount is high by weight, only a few metal particles were observed due to the high density of metal. When these samples were made, the metal was mechanically ground to a fine powder. The irregular and chip like shape of the mechanically powdered metal is seen in the micrograph.

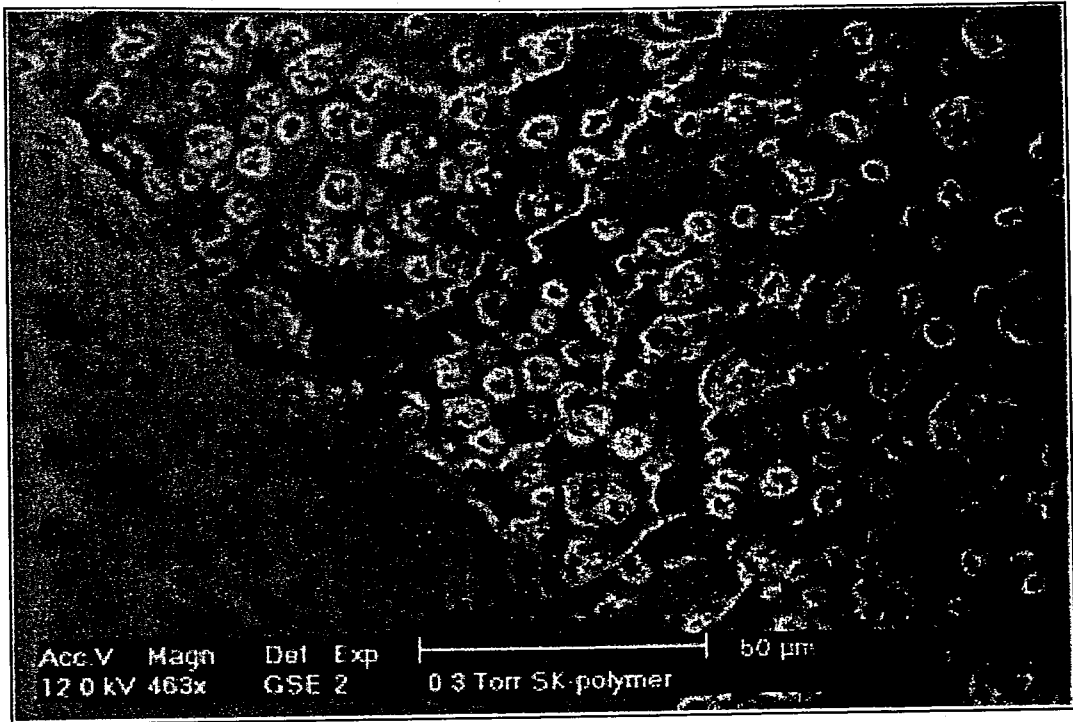


Figure 3.28. SEM image of 20 per cent PEG filled polyester (463 X)

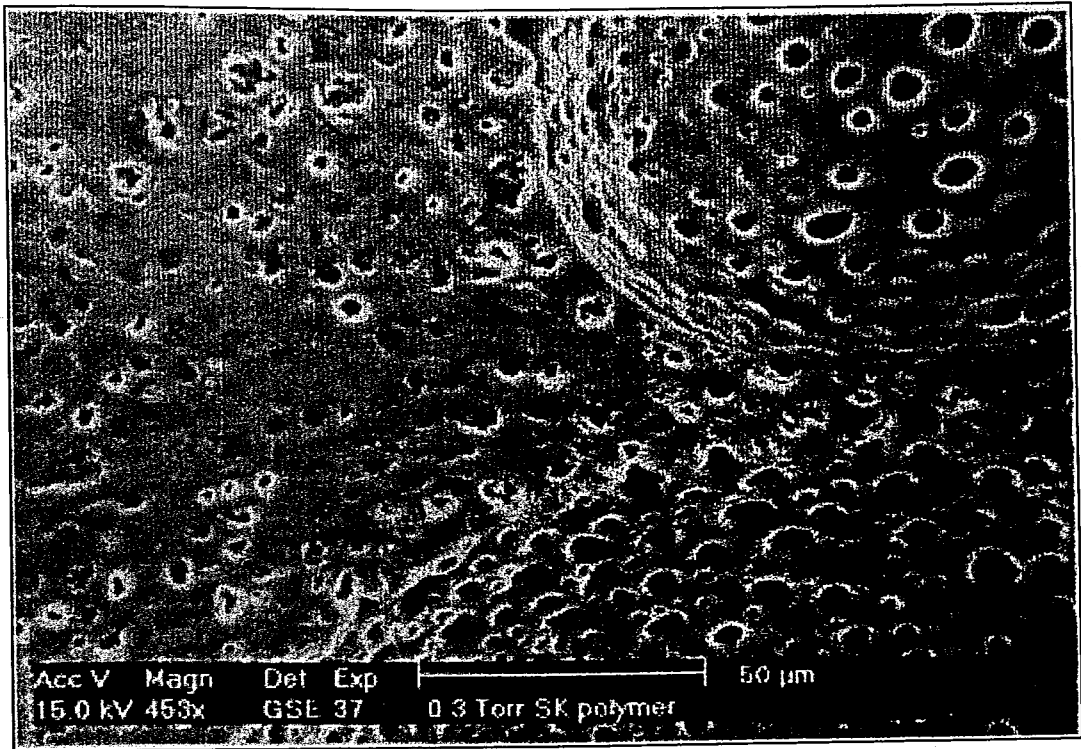


Figure 3.29. SEM image of 20 per cent PEG filled polyester (453 X)

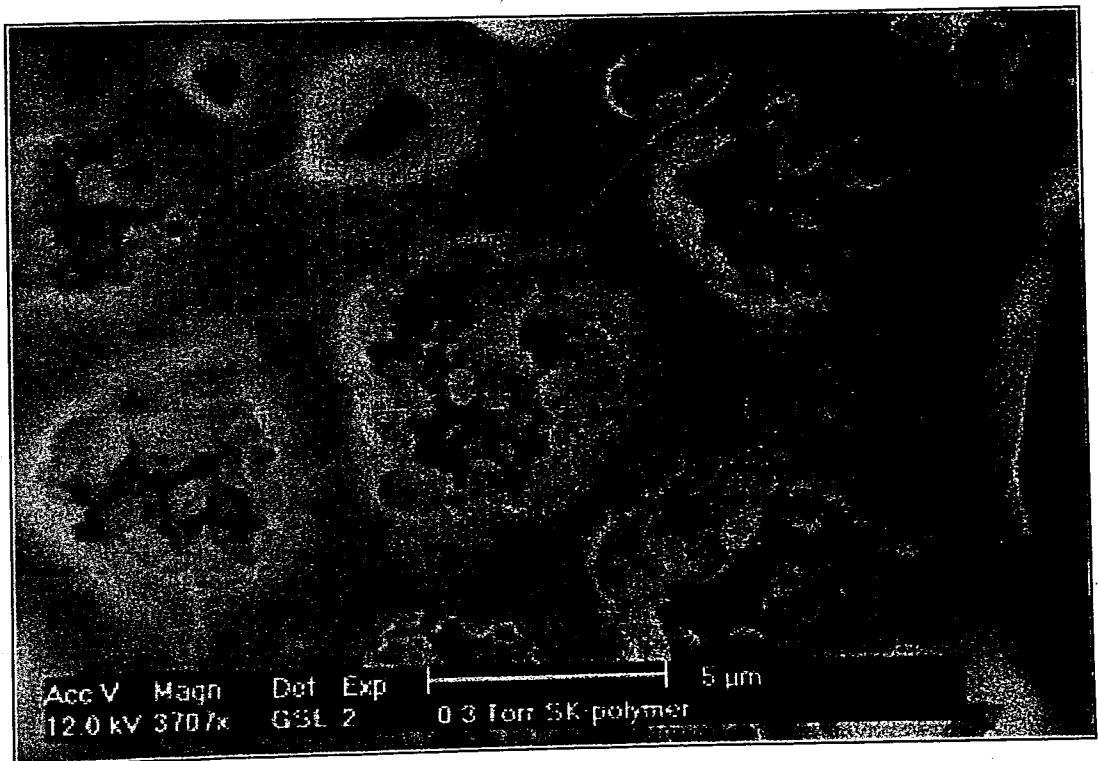


Figure 3.30. SEM image of 20 per cent PEG filled polyester (3707 X)

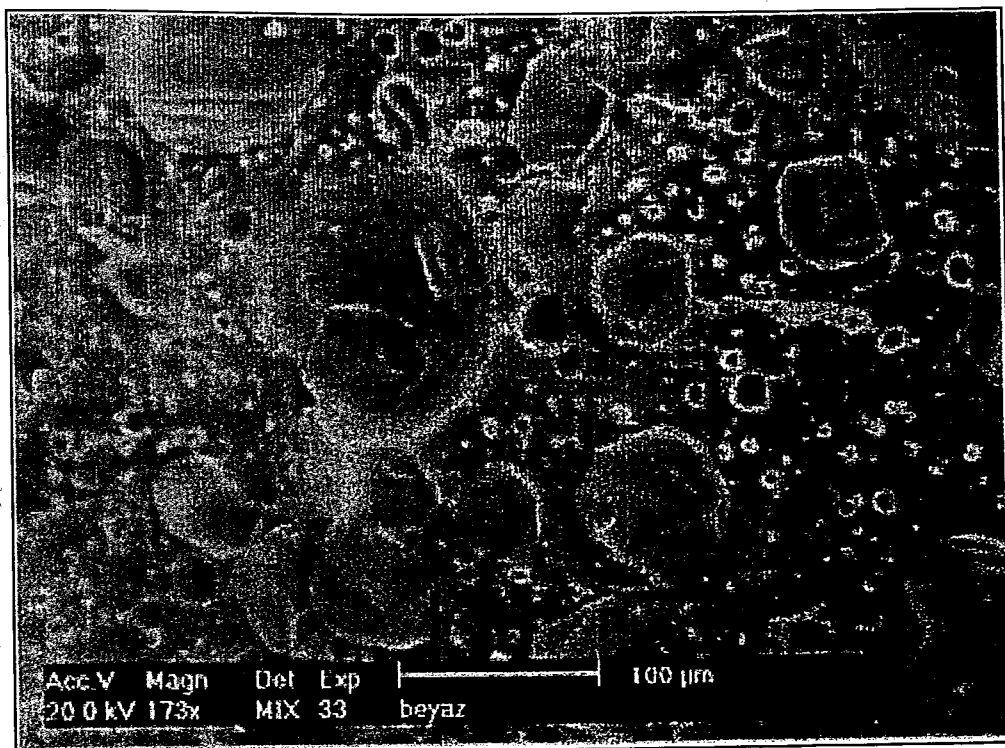


Figure 3.31. SEM image of 30 per cent paraffin filled polyester (173 X)

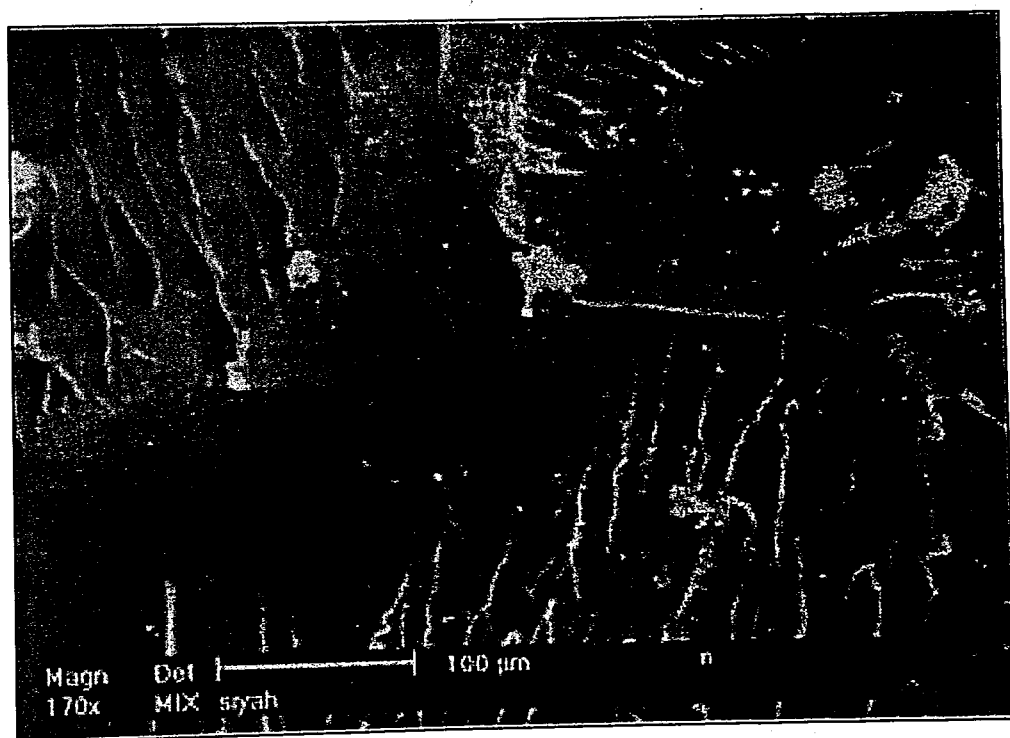


Figure 3.32. SEM image of 30 per cent metal filled polyester (170 X)

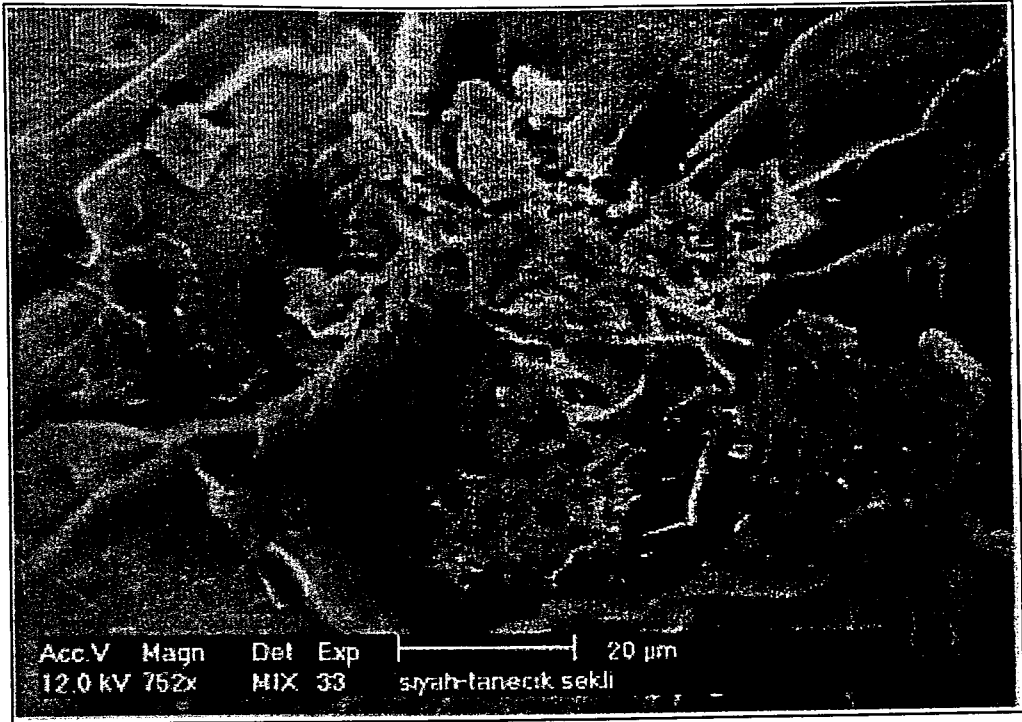


Figure 3.33. SEM image of 30 per cent metal filled polyester (752 X)

4. EXPERIMENTS

4.1. Chemicals and Apparatus

4.1.1. Chemicals

Chemicals that are used in this research are given in Table 4.1.

Table 4.1. Chemicals and suppliers

| Chemical | Composition | Supplier |
|-------------------------------|---|-----------------------------|
| MEKP | | Akzo-Nobel |
| 6 per cent cobalt naphthanate | Cobalt salts of substituted cyclopentane and cyclohexane carboxylic acids | Akzo-Nobel |
| PEG-4000 | Polymer of ethylene glycol | Fischer Scientific |
| Wood's Metal | An alloy (4 parts Bi, 2 part Pb, 1 part Cd and 1 part Sn) | Mallinckrodt Chemical Works |
| Paraffin | Mixture of hydrocarbons | Harleco |
| PEG-300 mono oleate | A nonionic surface active agent | Cam Elyaf A.Ş. |
| Stearic acid | A saturated long chain organic acid | Fischer Scientific |

Unsaturated polyester with brand name of CE 92 N8 was used. It includes 42 per cent styrene, reactive diluent and it is the product of Cam Elyaf A.Ş. Turkey. Specifications of the resin are given in table 4.2. This resin is composed of monomers maleic anhydride, phtalic anhydride, propylene glycol, and ethylene glycol.

4.1.2. Apparatus

Glass vials were used for preparing the samples with Wood's metal. Simple cavity molds made of a plastic were used for preparing samples with PEG-4000 and paraffin. Dynamic mechanical thermal analyses (DMTA) of samples were performed using a Polymer Laboratories Dynamic Mechanical Analyzer. Samples having dimensions about 100 mm x 150 mm x 2 mm were scanned at the frequency 1 Hz and heating rate 5 °C/min. Thermal behaviors of all samples were scrutinized by Differential Scanning Calorimeter (DSC) from Rheometric Scientific. Heating rate was 5 °C/min. Magnified views of samples were obtained on a Philips Scanning Electron Microscope (SEM). Finally, surface hardness of samples was determined by using Shormeter D, from Zwick.

Table 4.2. Properties of UPE CE 92 N8

| Specifications | Units | Values |
|----------------|-------------------|-------------------|
| Appearance | ----- | Clear |
| Density | g/cm ³ | Min 1,10 max 1,15 |
| Solid content | % | 58 |
| Acid number | mg KOH/gr | Max 25 |
| Viscosity | cps | Min 340- Max 460 |
| Gelation time | Minute | Min 6- Max 10 |
| Stability | Day | 67 |

4.2. Emulsion and Sol Preparation

4.2.1. Preparation of Paraffin Sols

There were 2 methods used for preparing paraffin sols. In the first method UPE and fillers were weighed. Then they were heated to 70°C and mixed and surface active agent added. After that, this mixture was cooled to room temperature while being stirred (Figure 3.1).

In the second method, molten paraffin was mixed with water and surface active agents was slowly added to this mixture with high speed stirring. By adjusting stirring rate paraffin emulsion with the desired particle size distribution was obtained. Then this emulsion was cooled to room temperature with continuous stirring. Cooled paraffin sol was filtered and dried. Then the paraffin powder was mixed with UPE (Figure 3.2) and a very stable sol (O/O sol) was observed.

4.2.1.1. Trial with Cu (II) Stearate. Cu (II) Stearate is both soluble in paraffin and UPE. 0.2 grams of Cu Stearate was mixed with 10 grams of paraffin at 70 °C and then this mixture was added to 10 grams of UPE at 70 °C. After a certain time, Cu stearate completely passed to UPE phase and a phase separation was observed.

4.2.1.2 Trial with PEG-300 Monooleate. 1 g of PEG-300 monooleate was taken and mixed with 10 grams of liquid paraffin at 70 °C. A clear solution was observed. Then 10 g of UPE was added to this solution. After cooling, a suspension that had nonuniform and rough particles was observed.

5 grams of Peg-300 monooleate was mixed with 10 g of melted paraffin at 70 °C. And then 10 g of hot UPE was added to this mixture and. Very rough dispersion was obtained.

4.2.1.3. Trial with Oleic and Stearic Acids. Oleic and stearic acids are soluble in paraffin but not soluble in UPE. 1 gram oleic acid was mixed with 10 grams of UPE at 70 °C, a cloudy solution was obtained. After a certain time, oleic acid separated.

1 gram stearic acid was dissolved in 10 grams of UPE at 70 °C. When this solution was cooled, stearic acid separated from UPE.

4.2.1.4. Trial with Quaternary Ammonium Salts. 5 g of hexadecyl-trimetyl ammonium chloride and 10 grams of paraffin were mixed at 70°C and a clear solution was obtained. This solution was mixed with 10 grams of UPE at 70°C. An unstable emulsion was observed. When this emulsion was cooled while stirring, phase separation was observed.

0.4 g of hexadecyl-trimethyl ammonium chloride and 4 grams of paraffin were mixed at 70 °C and then 0.1 g NaOH, and a few drop of water was added. A fish like smell was observed (this indicates presence of free amine). Then 4 grams of UPE was added to this solution at 70 °C, with continuous stirring. The resulting emulsion showed a phase separation during cooling. When separated paraffin phase weighted, it was found that 0.09 g of paraffin had dissolved in the UPE phase (5 per cent paraffin-UPE sol)

4.2.1.5. Trial with Pine Oil. 5 g of pine oil and 10 grams of paraffin were mixed. A creamy solid was observed. This solid was melted and mixed with 10 grams of UPE 70 °C. Phase separation of hot mixture was observed when stirring was stopped. When emulsion was cooled to room temperature while being stirred, a sol was formed. After 5-6 hours, phase separation was observed.

When a surface active agent such as liquid detergent, and a few drop of water were added to this paraffin sol. It gives extra stability to this sol.

4.2.1.6. Trial with Sodium Stearate. 10 grams of paraffin and 20 grams of water were heated together. Paraffin melts, 0.5 gram sodium stearate was added to this mixture until first bubbles was observed. Then this emulsion was cooled to room temperature while being mixed. After cooling, a paraffin sol was formed. This sol was filtered and the paraffin powder obtained was dried at room temperature.

Dried paraffin powder, were mixed with UPE in different amounts. After adding a few drop of water very stable paraffin sol was formed.

4.2.2. Preparation of PEG-4000 Emulsions

For 5 per cent PEG-4000 emulsion, 1 g of PEG-4000 were taken. It was dissolved in 0,5 g of water. Then this solution was mixed with 18,5 g of UPE. This mixture was stirred about 20 minutes. An emulsion was formed. The emulsion was milky and this emulsion was stable for a few hours. PEG, water, and UPE amounts used are shown in Table 4.3.

4.2.3. Preparation of Wood's Metal sols

Wood's metal was mechanically ground by a powered grinder. Mechanically ground metal dust was used for these sols. For 5 per cent metal sol, 0,25 g of metal powder was taken and mixed with 4,75 g of UPE. This sol was very unstable because of the density of the Wood's metal.

Table 4.3. Content of PEG-4000 emulsions

| PEG-4000 per cent of emulsion | PEG-4000 content | Water content | UPE content |
|----------------------------------|------------------|---------------|-------------|
| 5 per cent | 1 | 0,5 | 18,5 |
| 10 per cent | 2 | 1 | 17 |
| 20 per cent | 4 | 2 | 14 |
| 30 per cent | 6 | 3 | 11 |
| 40 per cent | 8 | 4 | 8 |

4.3. Curing of Samples

For all sols and emulsion, 0.5 per cent Co Naphtanate (based on UPE) and 1 per cent of MEKP (based on UPE) were used. The mixture was stirred and allowed to gel and cure in a mold. All samples were cured under normal atmosphere.

5. CONCLUSIONS

Cured thermoset polyesters with fillers made of phase change materials (PCMs) were prepared. PCMs used in this study were paraffin, PEG-4000 and Wood's metal uniformly and homogeneously scattered in polyester matrix.

In all sols and emulsions, unsaturated polyester is continuous phase and fillers are discrete phase. For PEG-4000 emulsions, up to 40 per cent (w/w) emulsions were prepared. For paraffin case, up to 50 per cent sols were prepared. For Wood's metal sols, 80 per cent sol could be prepared. For all emulsion and dispersions viscosity of system was increased with the increasing amount of filler.

The production of thermoset polyester is carried out by free radical cross linking of the continuous phase. Suitable radical initiator was a liquid peroxides, Methyl ethyl ketone peroxide was at 1 per cent weight of resin. Cobalt naphthenate was used as an accelerator at 0.5 per cent weight of resin.

The mechanical properties of cured resins vary with PCM content. Paraffin causes sharp decreases in mechanical properties. Reduction of mechanical properties is sudden at 5 per cent paraffin content, then reduction gradually goes on at slower rate as the paraffin amount increases. PEG-4000 also causes decrease in mechanical properties but they are not as sharp as in paraffin case. Wood's metal does not cause a sharp reduction in mechanical properties at low percentages. In paraffin and Wood's metal filled samples, the filler is a load bearing component.

DMTA of cured samples show a reduction in glass transition temperature (T_g) when compared with neat polyester. At phase change temperatures of the fillers, the samples show observable changes in dynamic mechanical properties. For PEG-4000 and paraffin filled polyesters, even at 5 per cent filler amount sharp decreases in E' , E'' , and $\tan \delta$ values. However, for Wood's metal filled samples, these changes can be observed only at high metal percentages. Maximum working temperatures of cured samples decrease with

increasing filler amount. Moreover, abrupt changes were observed around melting point of fillers.

Neat polyester does not show any melting transition. However, paraffin and Wood's metal filled samples show melting transitions. PEG-4000 filled samples do not show melting transition because PEG-4000 is substantially soluble in polyester and it diffuses to polyester matrix.

Finally, it is obvious that around the melting point of fillers materials absorbs a certain amount of heat. Except PEG-4000 filled samples, paraffin and metal filled samples show endotherm around the melting point of filler while materials themselves show no indication of melting externally and retain their physical shape. We believe that with further work, intelligent materials that show a dramatic change in modulus at a desired temperature can be manufactured with phase changeable fillers.

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