MECHANICAL AND THERMAL PROPERTIES OF THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTER (TLCP) AND ITS MIXTURES WITH POLY(ETHYLENETEREPHTHALATE) AND DENTURE BASE POLY(METHYL METHACRYLATE)

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Prof. Dr. Canan ÖZGEN
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Sciences

Prof. Dr. Ali USANMAZ
Head of Department

This is to certify that we have read this thesis and that in our opinion it's fully adequate, in scope and quality, as a thesis for the degree of Master of Science in Polymer Science and Technology

Prof. Dr. Ali USANMAZ
(Supervisor)

Examining Commitee in Charge

Prof. Dr.Ali USANMAZ (METU-PST)

Dr. A.Bedii ERDEMIR (METU-CHEM)

Prof. Dr.Arife DOGAN (GAZI UNI.DENTISTRY)

Prof. Dr.Duygu Kisakürek (METU-CHEM)

Assoc.Prof.Dr. Gülsün Gökagaç (METU-CHEM)

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ABSTRACT

MECHANICAL AND THERMAL PROPERTIES OF THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTER (TLCP) AND ITS MIXTURES WITH POLY(ETHYLENETEREPHTHALATE) AND DENTURE BASE POLY(METHYL METHACRYLATE)

ÖZTÜRK, Hale Bahar

M.Sc., Department of Polymer Science and Technology
Supervisor: Prof. Dr. Ali USANMAZ
Coadviser: Dr.A.Bedii ERDEMIR
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In this study, the thermal and mechanical properties of poly(ethylenetheraphthalate) (PET)-thermotropic liquid crystal polyester (TLCP), mixtures and poly(methyl methacrylate) (PMMA)-TLCP mixtures were studied. The curing of PMMA-TLCP mixtures was done by heat, gamma radiation and microwave. The amount of TLCP in mixtures was % 0.5, 2 and 5 TLCP by weight.

TLCP was synthesized by melt-acidolysis system, and PET-TLCP mixtures were prepared by using lab scale batch mixer. PMMA samples were prepared according to denture manufacturer’s procedure. The characterization of polymer samples and mixtures were carried by FT-IR, NMR, DSC, DMA, tensile, impact, three point bending tests and light microscopy.

The mixing of TLCP with PMMA yielded heterogeneous dispersions. This was observed from light micrographs. The mechanical and rheological properties of all polymers were not positively affected by inclusion of TLCP. It is also worthwhile to note that weakening of PET-TLCP mixtures were due to the thermal degradation as the thermal age of the mixtures is much higher.

Key words: Polymers, denture base materials, liquid crystalline polymers, PET, mechanical and thermal properties.

ÖZ

TERMOTROPIK SIVI KRISTAL KOPOLIESTERLER (TLCP) VE, TLCP ILE POLI(ETILENTEREFITALAT) (PET) VE PROTEZ KAIDE MATERYALI POLI(METIL METAKRILAT) (PMMA) KARISIMLARININ MEKANIK VE ISISAL ÖZELLIKLERI

ÖZTÜRK, Hale Bahar

YL., Polimer Bilimi ve Teknolojisi Bölümü
Danisman: Prof. Dr.Ali USANMAZ
Yardimci Danisman: Dr.A.Bedii ERDEMIR
Agustos 2004, 90 sayfa

Bu çalismada, PET-TLCP karisimlarinin ve isi, gama ve mikrodalga yöntemleri kullanilarak kürlendirilmis protez kaide materyali PMMA'nin TLCP ile karisimlarinin bazi özellikleri saptanmistir. TLCP, PET ve PMMA örneklerine agirlikça % 0.5, 2 ve 5 oranlarinda eklenmistir.

Bu amaçla, TLCP eriyik halde asitli ortamda sentezlenmis, PET-TLCP karisimlari batch mikserde, test numuneleri de karisim elde edildikten sonra kompres baski makinesinde hazirlanmistir. Üç farkli kürlesme metodu kullanilarak PMMA-TLCP karisimlari elde edilmistir. Protez kaide materyali PMMA örnekleri üretici talimatina göre hazirlanmistir. Polimer örnekleri ile karisimlarinin karakterizasyonu FT-IR, NMR, DSC, DMA, çekme testi, vurma testi, üç nokta egme testi ve optik mikroskop ile yapilmistir.

Optik mikroskop sonuçlarina göre, TLCP’nin PET ve PMMA ile karisimlari heterojendir. Polimerlerin mekanik ve reolojik özelliklerinde TLCP takviyesi ile iyilestirme görülmemistir. PET-TLCP karisimlarinin mekanik özelliklerindeki zayiflama isisal degredasyon yüzündendir.

Anahtar Sözcükler: Polimerler, protez kaide malzemeleri, sivi kristal polimerler, PET, mekanik ve isisal özellikler

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To my family.

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CHAPTER 1

INTRODUCTION

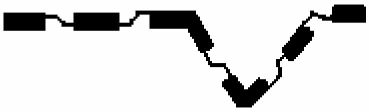
1.1 THERMOTROPIC LIQUID CRYSTALLINE POLYMERS (TLCPs)

Liquid Crystals (LC) are structures between a three dimensionally ordered crystal and a disordered fluid. There are 3 types of LC phases; smectic, cholesteric and nematic. Smectic phase has two dimensional order, nematic phase has one dimensional order. Cholesteric phases are similar to nematics, but they are layered. Molecules of each layer have a preffered direction along which they lay. Nematic phases are brought into existence either by strong polar solvents (lyotropic) or by action of heat (thermotropic) on suitably disrupted rodlike systems.

Rod like molecules of homo polymers form crystals with very high degree of perfection. Usually the heat required to melt these crystals is so high that thermal decomposition takes place before any melting occurs. For this reason a number of melting temperature depression techniques have been discovered. One or more of these methods is incorporated to the polymer chain by random co-polymerization. Melting temperature depression techniques are:

1. Introduction of flexible spaces

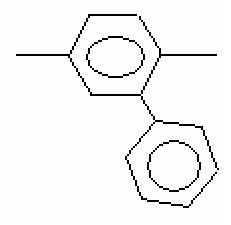
2. Use of kinks

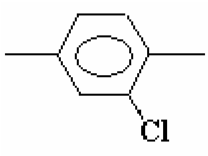


3. Use of mesogens with varying lengths

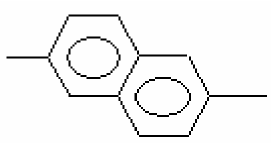
4. Varying the direction of ester link

5. Substituted aromatic residues



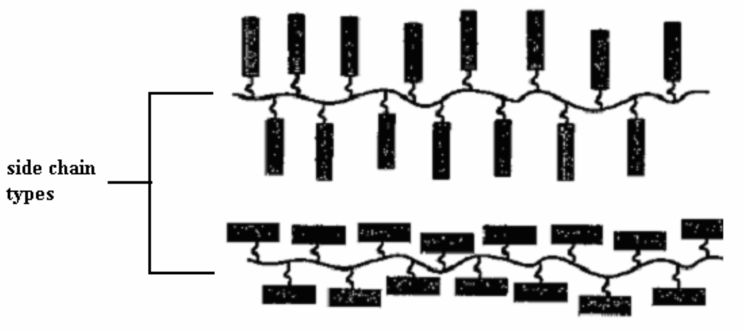


6. Naphtalane structures also disrupt perfection by non co-linear incoming and outgoing bonds they have [1].



The LC induction can be made by the main chain or side chains (Figure 1.1) [2]. In our study, we are interested in the nematic phases of linear thermotropic LC systems with flexible spacers. This TLCP was synthesized by reacting of poly(ethyleneterephthalate) (PET) as flexible spacer with p-acetoxybenzoic acid (p-ABA) in equal moles. p-ABA is able to polymerize by itself due to its functional groups so the expected system would be blocks of homo polymer of p-ABA seperated by blocks of PET [3].

a)



b)

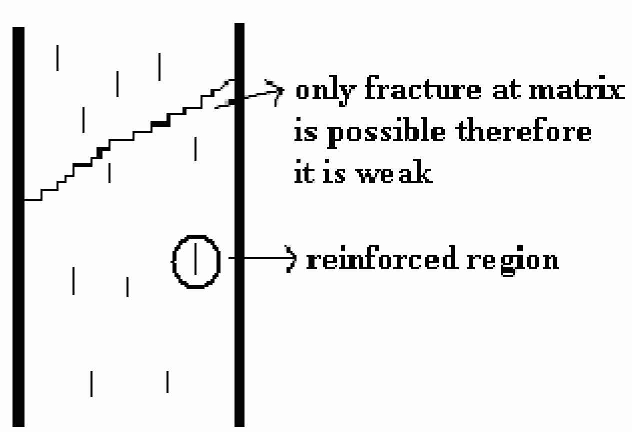
Figure 1.1 Main- and side- chain types of LCPs

TLCPs have received considerable attention since 1980s because of their special properties such as good heat resistance, flowability, dimensional stability, high modulus, strength, etc. However due to the imbalance in the cost, they are not very successful commercially. Also their high strength, high modulus properties are limited to fibrous form [4, 5].

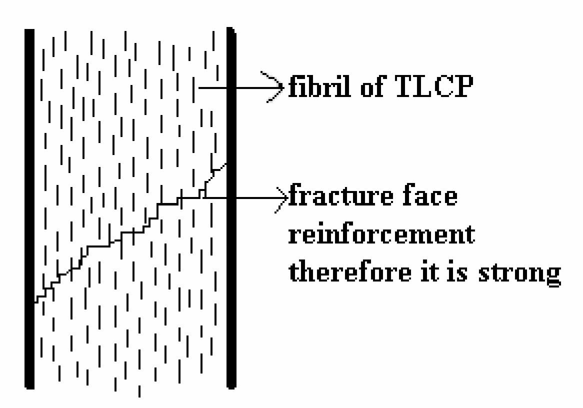
By blending thermotropic liquid crystalline polymers (TLCPs) with thermoplastics, either thermoplastic's properties prevail (Figure 1.2 a) or the reinforcing TLCP component's properties prevail (Figure 1.2 b). In Figure 1.2 a, no effect of reinforcement is seen for the mixture since reinforcement is confined to the region of rod. And the fibre will break where there is no rod in the polymer matrix. In Figure 1.2 b, the properties of TLCP determine the ultimate mechanical strength which is called as in-situ composites as the rigid TLCP domains elongate into fibrils under elongational flow during the processing operation.

Blend viscosities are greatly reduced by the addition of small quantities of the TLCP component so that processability is improved. The decrease of viscosity can make processable blend matrices, which otherwise can not be melt processed. The as-blended state of dispersion of the TLCP phase consists of spherical domains which deform during processing, forming long fibers with diameters of the order of microns or even smaller [6, 7, 8].

The abilities of LCPs as processing aids and reinforcing agents originate from their ability of in-situ forming of highly oriented fibrillar structures when subjected to elongational flows in molten matrix following extrusion. This property of LCPs makes them better reinforcing agents than glass fibers. The modulus of glass fibers is usually 86Gpa and the modulus of drawn LCPs is up to 105 GPa which depends on processing histories of LCPs. Therefore, it is possible to use LCP as reinforcements instead of glass fibers. Because of these characteristics of LCP, polymer blends containing LCPs have received considerable interest. These blends have been considered in many areas including electronics, automotive, aviation industry, medical, etc [9, 10].



a)



b)

Figure 1.2 Thermoplastic polymer-TLCP blend in fibrous form
a) Thermoplastic's properties prevail b) TLCP properties's prevail

1.1.1 The rheology of TLCPs

As shown in Figure 1.3, in Newtonian behaviour, viscosity does not change with shear rate. In dilatant behaviour, viscosity increases with shear rate where concentrated suspensions show this behaviour. In pseudoplastic behaviour, viscosity decreases with shear rate where polymer melts generally show this behaviour. Unlike isotropic polymers, TLCPs consist of a shear-thinning even at very low shear rates.

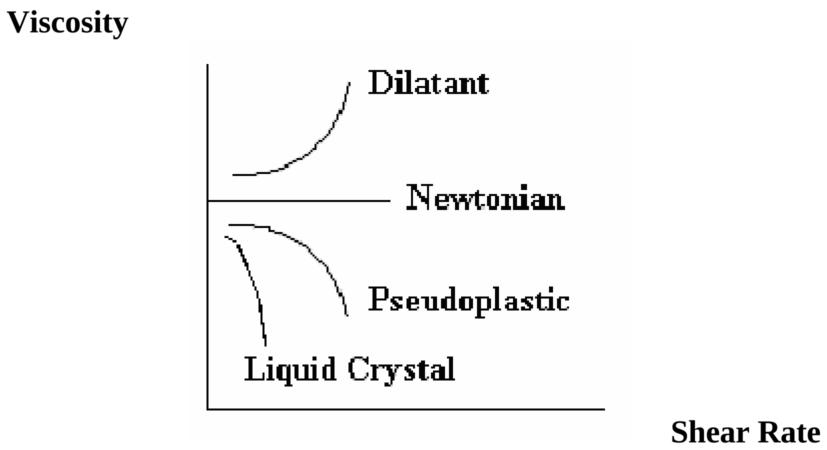


Figure 1.3 Scheme of the flow curves

As the TLCP undergoes a crystal to nematic transition with increasing temperature, the viscosity decreases. The ordered TLCP chains align in the flow direction and the flow is much easier than in the isotropic phase. All of the uses of TLCPs rely on the short-range order and anisotropy of the TLCPs' nematic domains. Under elongational flow, these domains take on long range order, align with each other and elongate into fibrils. After solidification, TLCP improves the mechanical and barrier properties of a thermoplastic. [11, 12, 13].

1.2 POLY(ETHYLENE TEREPHTHALATE) (PET)

PET (Figure 1.4) is an important commercial polymer and it is suitable for the manufacture of textile fibers, beverage-bottles, food packaging, cord fabrics for car tyres, conveyor belts and other laminated and coated substrates, films (magnetic recording tape and photographic and x-ray films) and many other applications [14].

PET has high strength, rigidity and toughness, excellent dimensional stability, low coefficient of friction, high transparency and good resistance to water, chemicals and grease, but it is moisture sensitive in the molten phase and should be dried prior to final processing to ensure optimum physical properties of the final properties. Alkaline solutions dissolve PET.

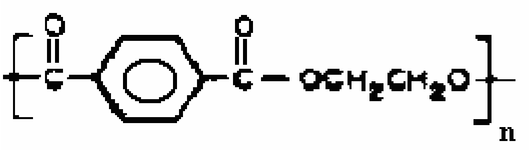


Figure 1.4 Chemical structure of PET

Polyesters are linear polymeric molecules containing in-chain ester groups, formally derived by condensation of a diacid with a diol. PET is a semi-crystalline homopolymer [15].

Polyesters were initially discovered and evaluated in 1929 by W.H. Carothers, who used linear aliphatic polyester materials to develop the fundamental understanding of condensation polymerization, study the reaction kinetics, and demonstrate that high molecular weight materials were obtainable and could be melt-spun into fibers [16].

In the late 1980s, new fully aromatic polyester fibers were introduced for use in composites and structural materials. In general, these materials are thermotropic liquid crystal polymers that are melt-processible to give fibers with tensile properties and temperature resistance considerably higher than conventional polyester textile fibers [17].

1.3 POLYMERS IN PROSTHETIC DENTISTRY

Polymers are used in the manufacture of denture that rest on the soft tissues of the mouth, artificial teeth, tooth restorative plastics, repair materials, orthodontic splints, bridge restorations [18]. The most commonly used polymer in prosthesis is acrylic resin, based on poly(methyl methacrylate) which represents 95 % of the plastics used in prosthetics. The general properties of the denture base materials should be as follows:

1. Adequate strength and durability,
2. Processing accuracy and dimensional stability in or out of oral fluids (i.e, it should not expand, contract or warp during processing and subsequent use by the patient)
3. Good chemical stability for both processed and unprocessed material
4. High surface hardness and low specific gravity
5. Satisfactory thermal properties (its softening temperature should be well above the temperature of any hot foods or liquid taken into the mouth).
6. Insolubility or no sorption of oral fluids present in the mouth
7. Absence of taste, odor, oral tissue irritation and resin should be non toxic
8. Natural appearance (color and translucency)
9. Stability of color of translucency
10. Reasonable adhesion to plastic, metal and porcelain
11. Easy and accurate fabrication and repair
12. Moderate cost

None of the acrylics or other plastics possess all the desired properties shown in this list. However, poly(methyl methacrylate), is the ideal material in denture bases to meet most of these requirements [19].

Before the acrylic polymers have been introduced to dentistry in 1937, materials such as porcelain, vulcanite, cellulose products, phenol formaldehyde and vinyl plastic had been used for denture bases. Each of these materials has properties that make them undesirable for use them as a denture resin [20].

1.3.1 Commercial Acrylic Resins as Dental Material

Acrylic resins used as the denture materials have been supplied in a variety forms, such as powder-liquid, gels, and sheets or blanks. Currently the powder-liquid type is the most popular. The powder-liquid type contains the materials listed in Table 1.1.

Table 1.1 Principal Ingredients of Denture base Powder and Liquid

Powder	**Liquid**
Acrylic polymer beads	Monomer
Initiator	Inhibitor
Pigments	Accelerator
Dyes	Plasticizer
Opacifiers	Crosslinking Agent
Plasticizer	
Dyed organic fibers	
Inorganic particles	

Most commercial materials contain PMMA as powder, which may have been modified with small amounts of ethyl, butyl or other alkyl methacrylates to produce somewhat softer polymer. The PMMA particles are usually spherical and are of different sizes. In the applications of dentistry, some additives are added into it: Diisobutylazonitrile [$CH_3C(CH_2)CH_2CN$], or commonly benzoyl peroxide [$(C_6H_5COO)_2$], is used as initiator. The amount of peroxide added is about 0.5-1.5 %. Initiator decomposed by heat or chemicals initiates the polymerization of the monomer. Some pigments such as iron oxide, zinc oxide, mercuric sulfide, cadmium sulfide, cadmium selenide or carbon black are used to obtain the various tissue like shades. These may be locked into the polymer beads by addition during commercial polymerization, or they may be mechanically mixed with the polymer beads after polymerization. Dyes, as well as pigments, occasionally are used, but they are not satisfactory, since they tend to leach out of plastic by oral fluids. Dyed synthetic fibers are added to the dental material in order to simulate blood vessels underlying the oral mucosa. Nylon or acrylic fibers are the examples of dyed organic fibers. Inorganic particles such as glass fibers and beads, or zirconium silicate are also used for this purpose. These particles are usually treated with some coupling agent such as vinyltriethoxysilane in order to improve the wetting and bonding of the inorganic particles and plastic. Zinc or titanium oxide is added in small amounts to increase the opacity until the material has the approximate translucency of the oral mucosa, since pure processed polymer is transparent, but titaniumdioxide is the most effective.

Plasticizers such as dibutylphthalate [$C_6H_4(COOC_4H_9)_2$] or triphenylphosphate [$(C_6H_5)_3PO_4$] in the proportions of 8-10 % may be incorporated in the powder or the monomer. These plasticizers are added to polymer both to speed the rate at which the monomer dissolves the polymer and to produce a softer, more resilient final product. One disadvantage in using plasticizers is that they may be gradually leached out of the oral fluids. Morever, a highly plasticized polymer (more than 10 %) may break up in the mouth after it has been further plasticized by absorption of water. Finally, addition of some additives such as glass fibers and alumina whiskers increases the stiffness and decreases the thermal coefficient of expansion. Polyethylene woven yarn and polyamide fabric also have been used to reinforce crylic polymers.

Some inhibitors are added into the monomer to preserve the shelf life of this monomer, and to prevent premature polymerization. Hydroquinone is most commonly used and added in amounts of 0.003 % to 0.1 %. When polymerization is accomplished by chemical rather than by heat, tertiary amines such as N,N,dimethyl,para-toludiene [$CH_3(C_6H_4)N(CH_3)_2$], N,N-dihydroxyethyl-para-toluidine [$CH_3(C_6H_4)N(CH_2CH_2OH)_2$] are used. Low molecular weight esters, such as dibutyl phthalate is added into the monomer as a plasticizer to give resilient character to final products. A polymer may also be plasticized by addition of some higher esters such as butyl or acetyl methacrylate to methyl methacrylate. In this case the esters polymerize and form a more flexible plastic. This type of internal plasticizing does not leach out in the oral fluids, and the material remains flexible.
Some crosslinking agents may also be added to the monomer to ensure a more insoluble and dimensionally stable denture base, to increase its resistance to surface cracks or crazing. Organic materials such as glycol dimethacrylate is the most commonly used crosslinking agent and may be present in amounts of 2 % to 14 %. When its amount is greater than this, it affects tensile strength, transverse properties, or hardness of the acrylic resin [21, 22].

1.4 POLYMERIZATION TECHNIQUES OF ACRYLIC RESINS

1. Heat activated denture base resins,
2. Gamma rays activated denture base resins,
3. Microwave activated denture base resins,
4. Chemically activated denture base resins,
5. Light activated denture base resins.

For all of these technique, four stages can be identified during the physical interaction of the powder and liquid:

Stage 1. Sandy: The polymer gradually settles into the monomer to form a incoherent mass. In this stage, the mixture will not stick to the fingers and is sandy when touched.

Stage 2. Stringy: The monomer attacks the polymer by penetrating into it. In this stage, the mixture is characterized by stringiness and adhesiveness when touched.

Stage 3.Dough: As the monomer diffuses into the polymer, the mass becomes more saturated, smooth and doughlike. It doesn’t adhere to fingers when touched. While the mixture is in this stage, it is packed into the mold. The mixing jar should be closed while molding so that the waiting dough can be moldable for a longer time, otherwise the monomer evaporates easily and the dough in the mixing jar becomes rubbery which isn’t wanted for the molding phase.

Stage 4.Rubbery: The monomer disappears almost completely by evaporation and by penetration into the polymer. It is no longer plastic, and it can not be molded [23].

Any change in the dimension of denture base materials, during either processing is of considerable importance. Chemically activated acrylic is more dimensionally stable than heat activated acrylics. Microwave activated acrylic resin is the most dimensionally stable in denture bases, since there is less thermal change. A visible light activated resin is more dimensionally stable than a heat activated resin.

Water sorption of PMMA is fairly high (0.69 mg/cm^2). After it is stored in water until equilibrium, a sorption of about 2 % occurs. The absorption of water affects the dimensional stability. PMMA absorbs water slowly over a period of time and expands. The absorption is due to primarily to the polar properties of the resin molecules. The water penetrates between the molecular chains and forces them apart. Water acts as a plasticizer and assists in the relief of stress within the resin and some dimensional changes occur. But it absorbs less water than any other resin.

At ambient temperature PMMA is resistant to weak acids, weak alkaline solutions, aliphatic hydrocarbons, non polar solvents, grease, oils, water and detergents. It is not resistant to strong acids and bases, benzene, polar solvents, ketones, esters, ethers, aromatic or chlorinated hydrocarbons. Alcohol will cause crazing. Ethanol also functions as a plasticizer and can reduce T_g.

The shelf life, or useful storage time at room temperature, for denture base plastics varies considerably. Acrylic plastics packaged in the powder-liquid form have excellent shelf life, since the powder is almost in definitely stable and the liquid usually is adequately protected from polymerization during storage by a hydroquinone inhibitor. The vinyl plastics packaged as a gel in which monomer is in contact with the polymer must be stored at refrigerator [19].

1.5 AIM OF THE STUDY

The aim of this study was to synthesize thermotropic liquid crystalline copolyester (TLCP), and to observe reinforcing properties of TLCP in different commercial plastic materials. For this purpose PET and PMMA were tried. The TLCP in PET improve the spinning properties in textile industry in addition used as mechanical property modifier. There are many reinforcing agent used in denture PMMA materials. However, no study has been reported for TLCP. Therefore the effect of TLCP on different property of two important commercial polymer is tested in this study. For the testing methods FTIR, NMR, DSC, DMA, tensile, impact, three point bending tests and light microscopy are used to investigate property change of PET- TLCP and PMMA-TLCP mixtures with different concentration of TLCP.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Thermotropic Liquid Crystalline Copolyester (TLCP)

The liquid crystalline copolymer employed in this study were synthesized by copolymerizing poly(ethyleneterephthalate) and p-acetoxybenzoic acid (p-ABA).

2.1.2 Poly(ethylene terephthalate) (PET)

Fibre grade PET used in the chips form in the experiments was obtained from Yesim A.S. situated in OSB, Bursa. It contains titanium dioxide as delustrant. These chips were dried in a vacuum oven at 120ºC for 24 hours before used for the experiments.

2.1.3 The Heat Activated Acrylic Resins

QC 20 (De Trey, Dentsply, England) which was used in this study, was in powder-liquid forms.

2.1.4 Chloroform, acetic anhydride and other solvents

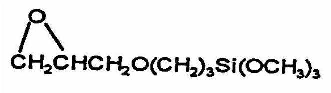
They were Merck grade and used without further purification.

2.1.5 Other materials used for the preparation of acrylic denture base

a. The Plaster
b. Modelling Wax
c. Cellulose Lacquers, it was used as a seperating agent
d. Polyethylene Thin Foil, it was used as an insulator

2.1.6 Silane Coupling Agent (SCA)

Received from HÜLS-VEBA Company, The SCA was Gamma-glycidoxypropyltrimethoxysilane (GLYM or A-187) [24].



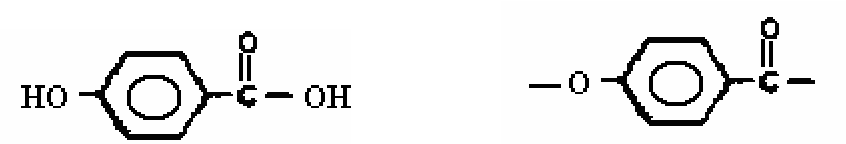
$CH_2CHCH_2O(CH_2)_3Si(OCH_3)_3$

2.2 APPARATUS

2.2.1 TLCP Synthesis Scheme

The experimental set up is given in Figure 2.2. The system consisted of 40 mm in diameter and 260 mm long glass polymerization tube, a custom built still head, a stainless steel helical stirrer and a silicon oil bath 150 mm deep. The still head at the top to support the stirrer bearing housing has three taps; for water condenser, nitrogen supply and vacuum pump connections. The silicon oil was placed in a 1.5 l capacity glass beaker supported by a jacket heater. A heating rate of 14°C/min could be achieved by jacket heater. The silicon oil temperature was monitored with a thermocouple. There are three traps between polymerization tube and nitrogen gas feeder so that oxygen or other impurities that can effect polymerization negatively could be trapped and also nitrogen gas feed ratio could be adjusted. There is one trap between polymerization tube and vacuum so that vacuum would not be affected by the by-products of the polymerization.

p-ABA was prepared by the acetylation of p-hydroxybenzoic acid (p-HBA) in a manner similar to the acetylation of salicylic acid. p-HBA (Figure 2.1) was added to acetic anhydride (140 ml) containing sulphuric acid (1.5 ml) at 60°C. The mixture was kept at 50-60°C for 30 minutes while being stirred. After cooling, the mixture was diluted with water (1500 ml) and filtered-off. The damp product was dissolved in hot ethanol (300 ml) and poured into water (750 ml) at 90°C. p-acetoxybenzoic acid was precipitated by cooling the solution. It was then filtered-off and washed with water before being dried under vacuum at 60°C for 24 hours. The melting temperature was measured by a hot stage microscope and found to be between 185°C and 187°C [1].



p-HBA

p-ABA residue in chain

Figure 2.1 Chemical structures of p-HBA and p-ABA residue in chain

The TLCP was synthesized from p-ABA and PET. All glassware used were flame dried. The dry monomers, 0.15 moles of each p-ABA and PET were charged directly into the polymerization tube and an excess of 35 ml of acetic acid was employed. The system was purged 3 times with nitrogen while stirring the slurry. After the completion of the purging operation, the system was placed into the preheated glass bath connected to a thermocouple, at 270°C while being swept with a continuous stream of nitrogen. The reaction mixture's temperature was increased to 295°C in 1.5 hours at atmospheric pressure. During this time, most of the acetic acid (both the excess and the reaction by-product) was collected via a condenser. Condenser valve was then closed and vacuum line was connected. The reaction mixture was maintained at the same temperature under vacuum for 30 minutes. The pressure in the reactor was reduced in two steps; first the by-product outlet valve was closed, the nitrogen feed was switched to the restricting capillary route, and the valve of the vacuum line opened slowly. The second step was carried out after about 3-5 minutes, the nitrogen valve was closed in order to cut off the nitrogen supply completely. The reaction was terminated by quenching the polymer tube in liquid nitrogen, after breaking the vacuum by nitrogen. p-ABA's chemical structure in TLCP is shown in Figure 2.1 (p-ABA residue in chain) [25, 26, 27].

PET-TLCP blends were prepared in the batch mixer of TLCP synthesis scheme under nitrogen at 290ºC for 5 minutes by % 0.5-2-5 TLCP additions. In order to prevent the phase separation of PET and TLCP, rapid heating and rapid solidification was done so that there will be no time for phase separation. The test samples were prepared by compression molding at 280ºC.

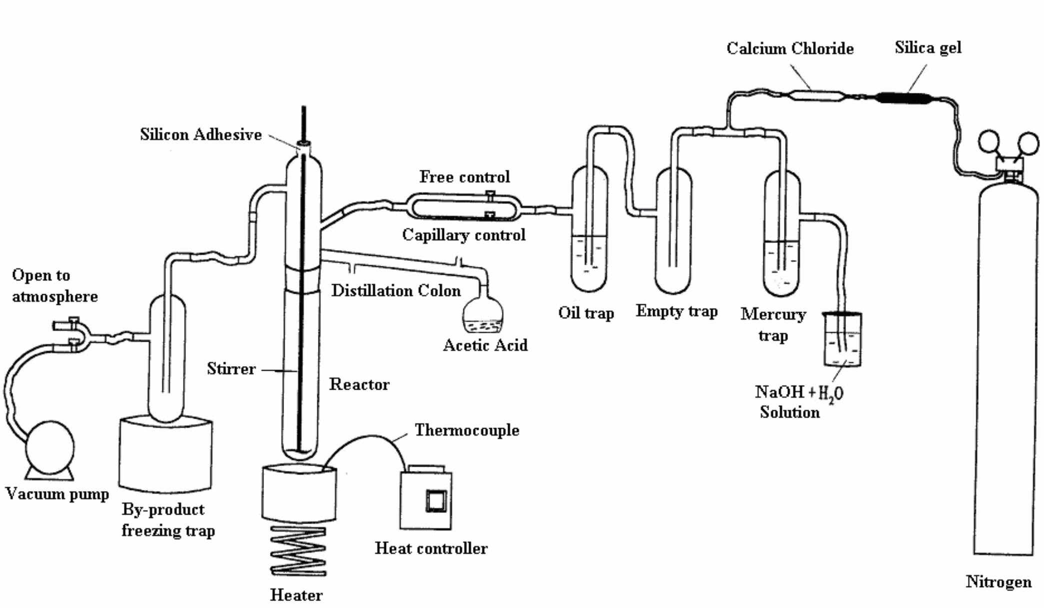


Figure 2.2 Schematic representation of the synthesis scheme of thermotropic liquid crystal polymer

2.2.2 Preparation of denture base PMMA-TLCP Mixtures

Firstly, the wax model was prepared, the investing material such as plaster was poured into the bottom half of the flask and the wax model was placed into the plaster. When the plaster was hardened, it was coated with a separating agent such as cellulose lacquers to provide insulation. The top half of the flask was seated, it was filled with a plaster. The flask was heated to soften the wax, it was flushed out with boiling water.

The test samples were prepared by using heat activated commercial materials by compression molding. The test samples were prepared by using heat activated commercial materials by compression molding. PMMA samples of denture materials were prepared according to a procedure given by manufacturer and samples were heat, microwave and gamma-cured. The procedure used was as follows:

a. TLCP was added in % 0.5-2-5 ratios and silane treated TLCP was added in % 0.5 ratio into the PMMA polymer (powder).
b. The plaster was prepared previously in another cup, and it was poured into the bottom of a flask, then the wax samples were placed in the plaster. Cellulose lacquer as a separating agent was used to insulate the surface of the plaster.
c. The top of the flask was seated, the flask was filled with the plaster and the lid was placed on it. Then it was kept under pressure for 5 minutes.
d. It was placed in hot water to soften the wax and the top and the bottom parts of the flask were separated. Any residual wax was flushed out with hot water. Constant temperature bath was accomplished by a closed Kotterman Labortechnik model, made of stainless steel.
f. The powder PMMA and liquid (methylmethacrylate monomer) were proportioned in the ratio of 3/1 in a glass beaker. The mixture was allowed to stand until a dough stage formed.
e. Then acrylic dough was packed into the flask and kept under pressure for 10 min. Afterwards it was placed in the water bath kept exactly at 60 °C for 30 minutes.
f. For heat curing, the bath's temperature was increased to 100 °C and the samples waited for 60 minutes.
g. For gamma curing, the samples were put into the Gamma radiation for 30 min, 90 min and 8 days. Radiation Source was 220 Model Gamma Cell' product of 'Atomic Energy of Canada Ltd.Co.'. The dose rate of source was about 15 krad/h during the experiments.
h. For microwave curing, the samples were put into the microwave oven (Arçelik, model MD 554) for 2 minutes at 600 watt.

2.2.3 Dynamic Mechanical Analyzer (DMA)

The rheological behaviour of the samples were recorded by TA-DMA 983 Dynamic Mechanical Analyzer. Heating rate was 5°C/min from 0 °C to 250 °C at a fix frequency of 0.3 Hz.

2.2.4 Differential Scanning Calorimeter (DSC)

Thermal properties of samples were analyzed by using Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S. All the measurements were done under N_2 atmosphere in a temperature range of 25ºC to 325ºC with 10ºC/min heating rate.

2.2.5 Impact Tests

For impact testing, denture base PMMA-TLCP were compression molded at room temperature. A pendulum impact testing machine, a Coesfeld PSW 4J, was used for the Charpy impact measurements with standard unnotched (nearly 3×7×60 mm) samples at room temperature. Charpy impact tests were performed according to the Test Method-I Procedure A in ASTM D256-91a (Standard Test Method for Impact Resitance of Plastics). At least 10 test specimens were used for each different type of blends.

2.2.6 Tensile Tests

Tensile tests were performed by a LLOYD LR 5K Computerized testing machine for all specimen groups. Tests were performed according to ASTM D638M-91a, (Standard Test Method for Tensile Properties of Plastics). The speed was 20 mm/min. 5 test specimens were used for each different type of samples.

2.2.7 Three point Bending Test

Three point bending measurements were carried out by using the LLOYD LR 5K Computerized testing machine for all specimen groups according to Test Method-I Procedure A of ASTM D790M-92 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics). At least five rod test specimens (80×10×3 mm) were tested for each different type of blends. Here, the widths and the thicknesses were also measured by using micrometer at their upper and lower points and their average values were determined.

The span length (L), the length of the test specimen between the lower supports of the apparatus, was 4 cm and the speed of testing was 10 mm/min. Stress is computed from the specimen thickness, the bending moment, the moment of inertia of the cross section. The maximum tensile stress exists at the bottom specimen surface directly below the point of load application. The load versus the deflection were plotted. The stress at fracture using this flexure test is known as the *flexural strength*. For a rectangular cross-section, the flexural strength, s_{fs}, is equal to:

$$s_{fs} = \frac{3F_f L}{2bd^2} \qquad (2.1)$$

where, F_f is the load at fracture (N), L is the distance between support points (mm), b is the width of the specimen (mm), and d is the depth of specimen (mm). The *maximum strain* in the outer fibers occurs at midspan, is calculated as follows:

$$r = \frac{6Dd}{L^2} \qquad (2.2)$$

where, r is the maximum strain in the outer fibers (mm/mm), D is the maximum deflection of the center of the beam (mm), L is the support span (mm) and d is the depth of specimen (mm).

Tangent modulus of elasticity (flexural modulus), E_B, (MPa) is the ratio, within the elastic limit of stress to corresponding strain and shall be expressed as MPa. It is calculated by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve and by using Equation (2.3)

$$E_B = \frac{L^3 m}{4bd^3} \qquad (2.3)$$

where, E_B is modulus of elasticity in bending (MPa), L is the length of support span (mm), b is the width of the beam tested (mm), d is the depth of beam tested (mm), and m is the slope of the tangent to the initial straight-line portion of the load deflection curve, N/mm of deflection [28].

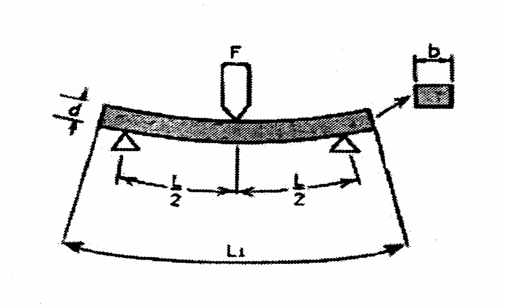


Figure 2.3 A three-point bending scheme

2.2.8 Infrared Spectrometer

Infrared spectra of monomer and the polymers obtained with different polymerization techniques were taken from KBr pellets by using Nicolet 510 FT-IR Spectrometer. The data was processed by the OMNIC computer program.

2.2.9 Nuclear Magnetic Resonance

Magnetic Resonance Spectrometer, Ultrashield 400 MHz Digital NMR Bruker, was to record ^{1}H and ^{13}C Spectra.

2.2.10 Light Microscopy

TLCP distribution in PMMA mixtures and the surface of these mixtures were examined under the light microscope. In this analysis, Prior Laboratory Microscope Model B 3000 was used. Microscope was connected online to a computer by Pro Series, high performance CCD camera. Images were seen alive in monitor by an analytical imaging software called Image Pro Plus 3.0 for Windows. The views of the samples were snapped and saved into the computer [29].

CHAPTER 3

RESULTS AND DISCUSSION

3.1 FT-IR ANALYSIS OF PET-TLCP MIXTURES

The FT-IR spectra of PET, TLCP and PET-TLCP composites containing % 0.5 – 2 – 5 TLCP are given in Figures 3.1-3.5. The peaks in spectrums are assigned as: 0-H around 3430 cm^{-1}, C-H aliphatic around 2970 cm^{-1}, H-C=O around 2910 cm^{-1}, ester stretching around 1720 cm^{-1}, C=C aromatic around 1572 cm^{-1}, C-H bending around 1410 cm^{-1}, O-H primary alcohol around 1021 cm^{-1}, C-H bonds around 666 cm^{-1} and 493 cm^{-1}. The observed peak at about 1681 cm^{-1} in PET-p-ABA spectra proves ester exchange reactions between ester groups of PET and p-ABA (Figure 3.2) [13]. The copolymer was shown by DSC thermogram to contain two segments in a block copolymer (Figure 3.7).

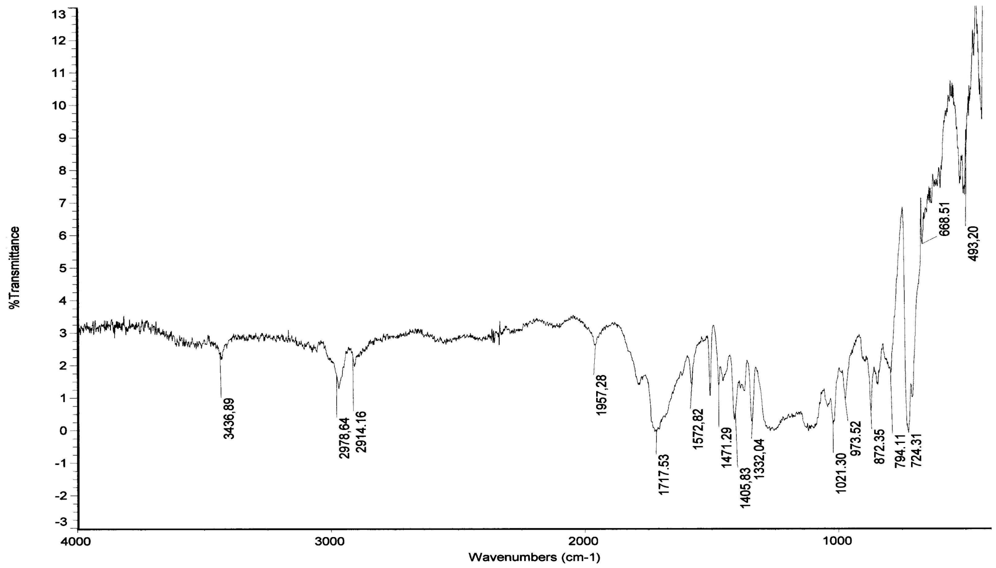


Figure 3.1 FT-IR Spectrum of PET

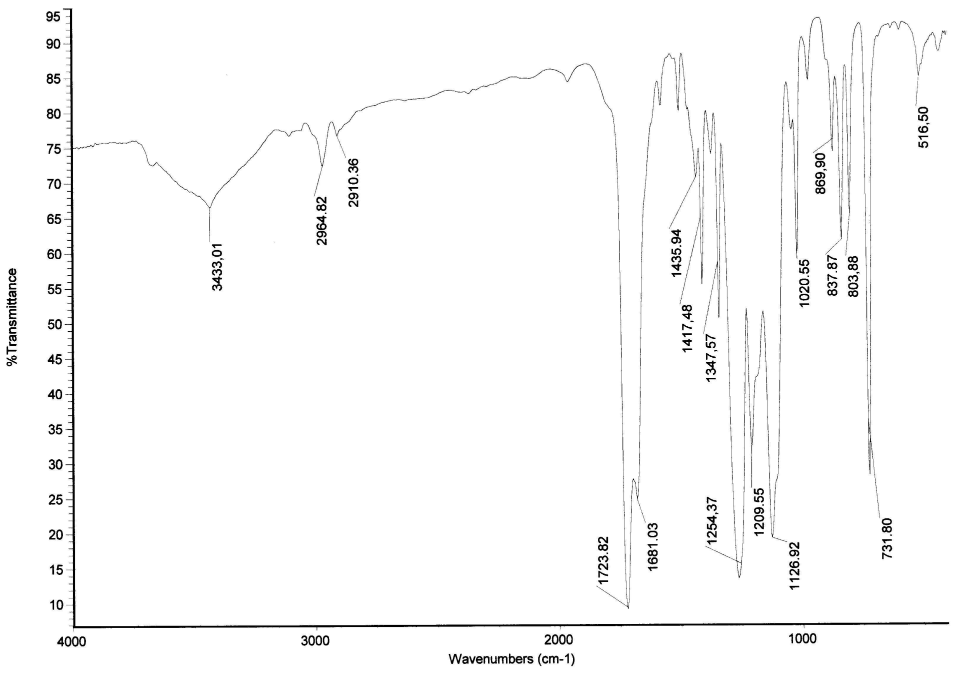


Figure 3.2 FT-IR Spectrum of TLCP

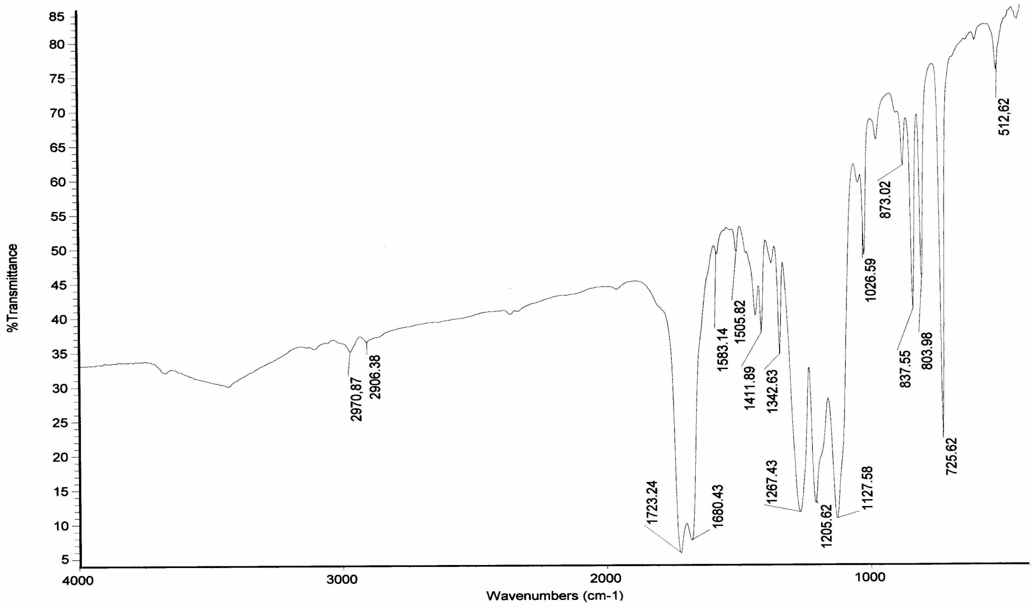


Figure 3.3 FT-IR Spectrum of PET- % 0.5 TLCP mixture

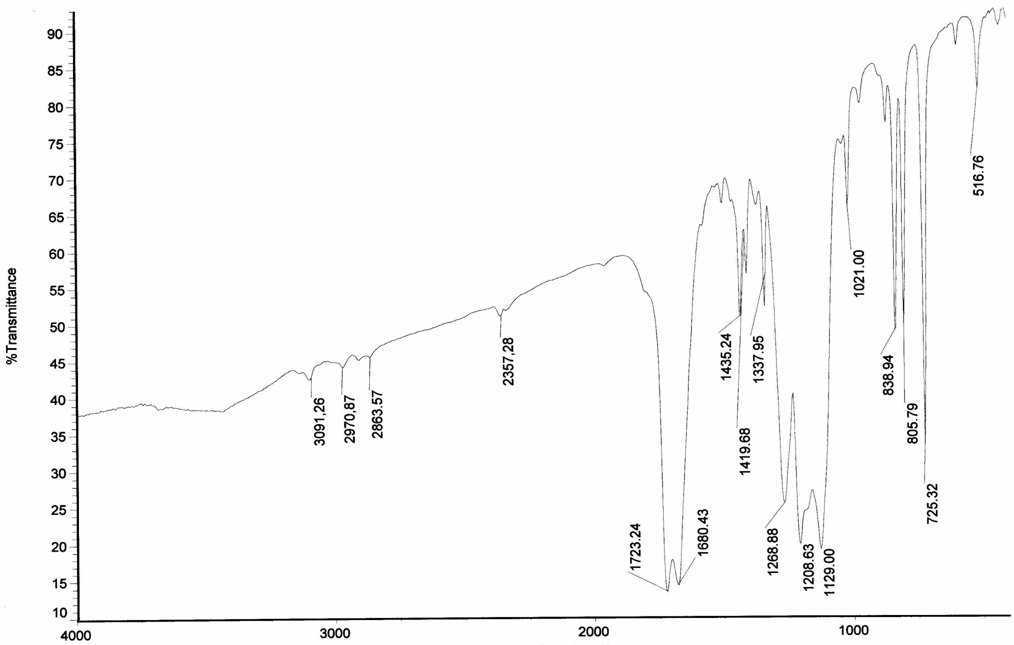


Figure 3.4 FT-IR Spectrum of PET- % 2 TLCP mixture

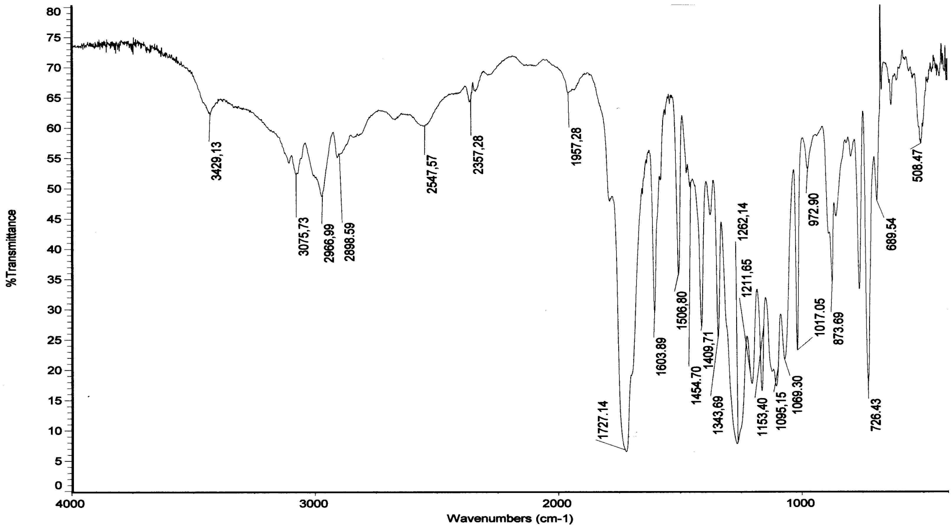


Figure 3.5 FT-IR Spectrum of PET- % 5 TLCP mixture

3.2 DSC ANALYSIS OF PET-TLCP MIXTURES

The DSC thermograms of PET, TLCP and PET-TLCP composites containing % 0.5 – 2 – 5 TLCP are given in Figures 3.6 - 3.11.

In the DSC thermogram of PET (Figure 3.6) T_g is observed at 60°C, T_c at 98°C and T_m at 256.3°C. Between T_g (60°C) and T_c (98°C) a broad peak over the baseline was observed. At T_g, the curve should give an inclination then continue with a straight line. Since the crystallization starting at this region also will make a exothermic peak increase the level of baseline, which makes the reading of T_g difficult.

The DSC thermogram of TLCP (Figure 3.7) showed two T_g at 50.7°C and 154.7°C corresponding to PET and PABA polymer segments, respectively. The smaller T_g value for PET (50.7°C instead of 60°C) is due to the smaller segmental chain of PET in copolymer (TLCP). Since there is one T_m (319.5°C multi) in TLCP thermogram (Figure 3.7), this might be due to the nature of PET that does not give crystalline phase when heated or cooled fast. The observed value belongs to that of p-ABA segments. Since the chain length of segments are not uniform instead of a single T_m peak, multi peaks close to each other were observed.

In Figures 3.8 (% 0.5 TLCP), 3.10 (% 2 TLCP) and 3.11 (% 5 TLCP), crystallization peak is observed in each of thermograms at 125-129°C. However in Figure 3.9 (% 0.5 TLCP), no crystallization peak is observed. This is because the sample used in Figure 3.9 was already in crystalline form, further crystallization was not observed in this case. The results are also tabulated in Table 3.1. The PET-TLCP mixtures's T_m are slightly lower than that of PET. In these thermograms the T_m for p-ABA is not observed, because the percentage composition of p-ABA in mixture is very small.

During the preparation of PET-TLCP mixtures via batch mixer, viscosity decrease was observed with the addition of TLCP at any quantity. This is due to the rigid rodlike molecular structure of TLCP, which are aligned in the flow direction at about the melting temperature.

Table 3.1 DSC results of PET and PET-TLCP mixtures

	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C)
PET	60	98	256.3	
TLCP	50.7 – 154.7	-	319.5	-
PET - % 0.5 TLCP Non-crystallized mixture	78.5	129.5	254.2	-
PET -% 0.5 TLCP Crystallized mixture	-	-	252.6	-
PET - % 2 TLCP mixture	77.3	127.6	255.2	-
PET - % 5 TLCP mixture	76,8	125,2	255.7	-

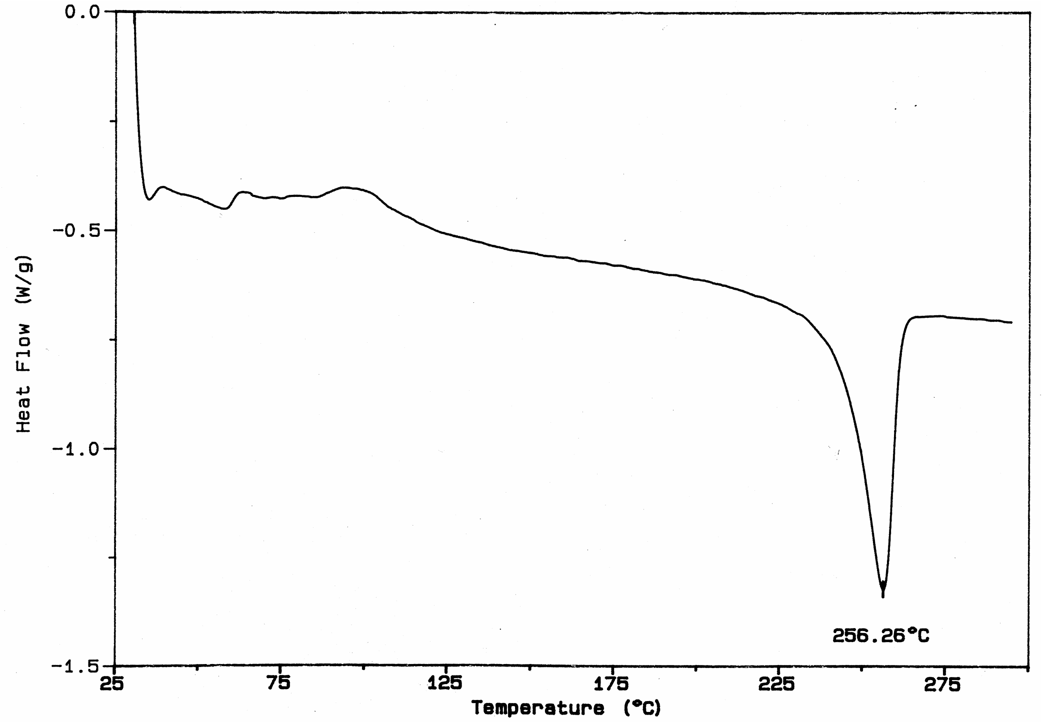


Figure 3.6 DSC Thermogram of PET

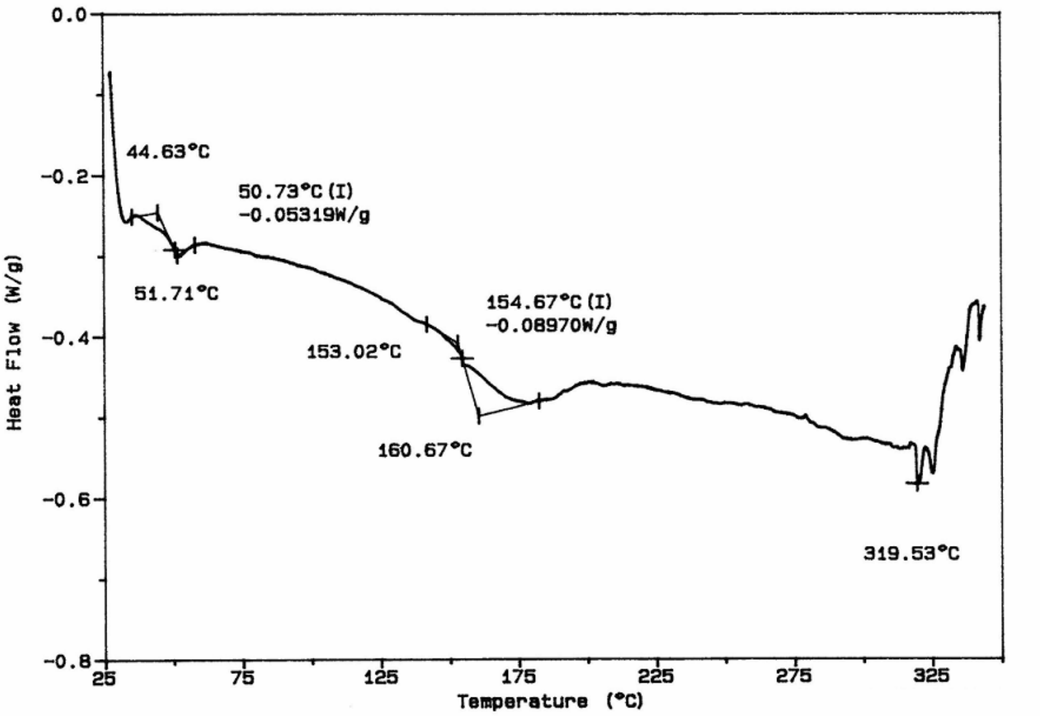


Figure 3.7 DSC Thermogram of TLCP

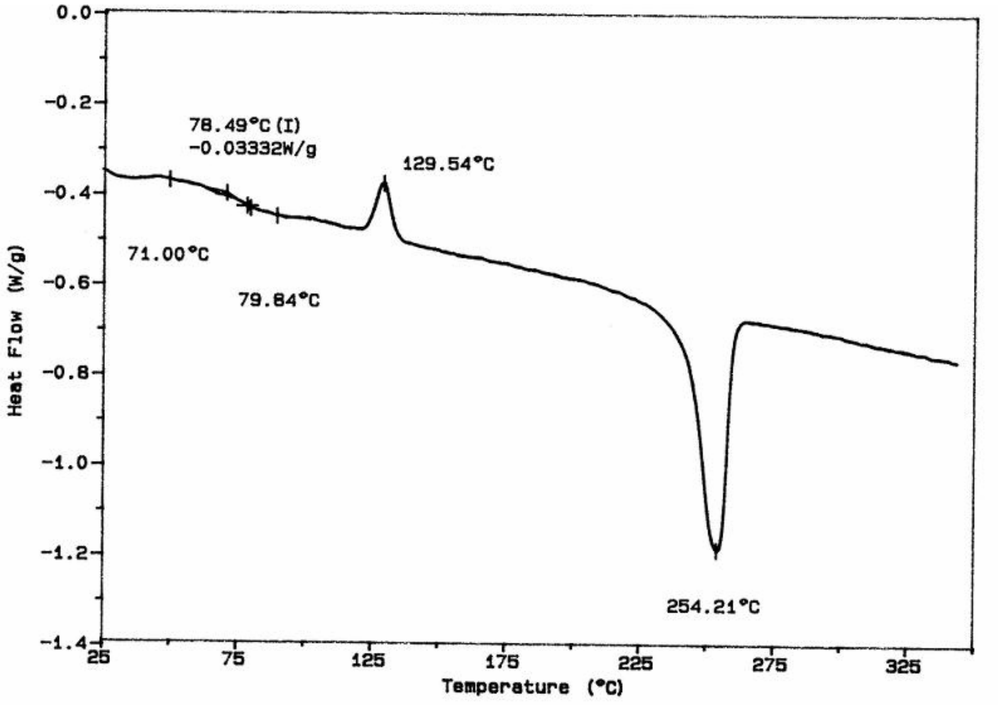


Figure 3.8 DSC Thermogram of non-crystallized PET-% 0.5 TLCP mixture

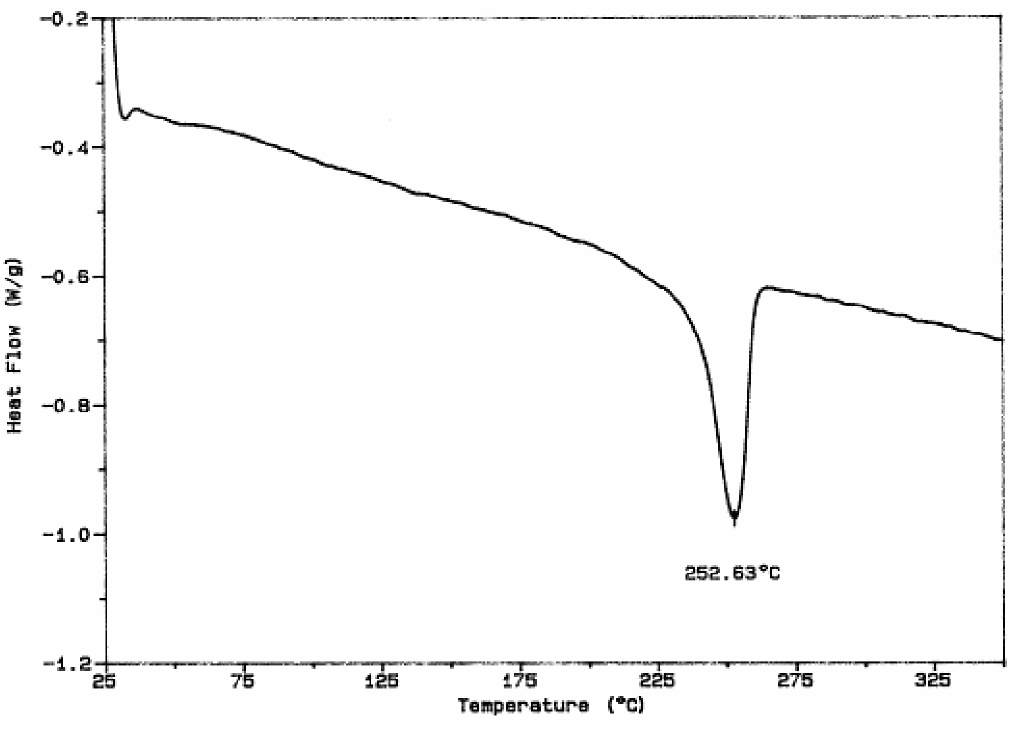


Figure 3.9 DSC Thermogram of crystallized PET-% 0.5 TLCP mixture

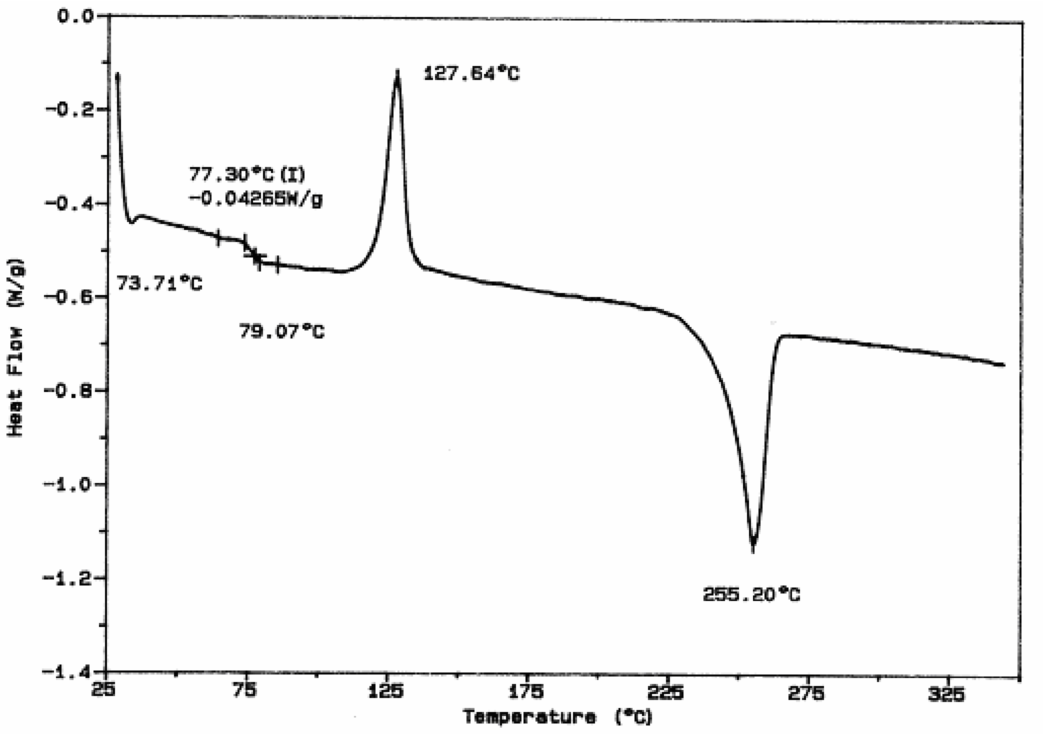


Figure 3.10 DSC Thermogram of PET-% 2 TLCP mixture

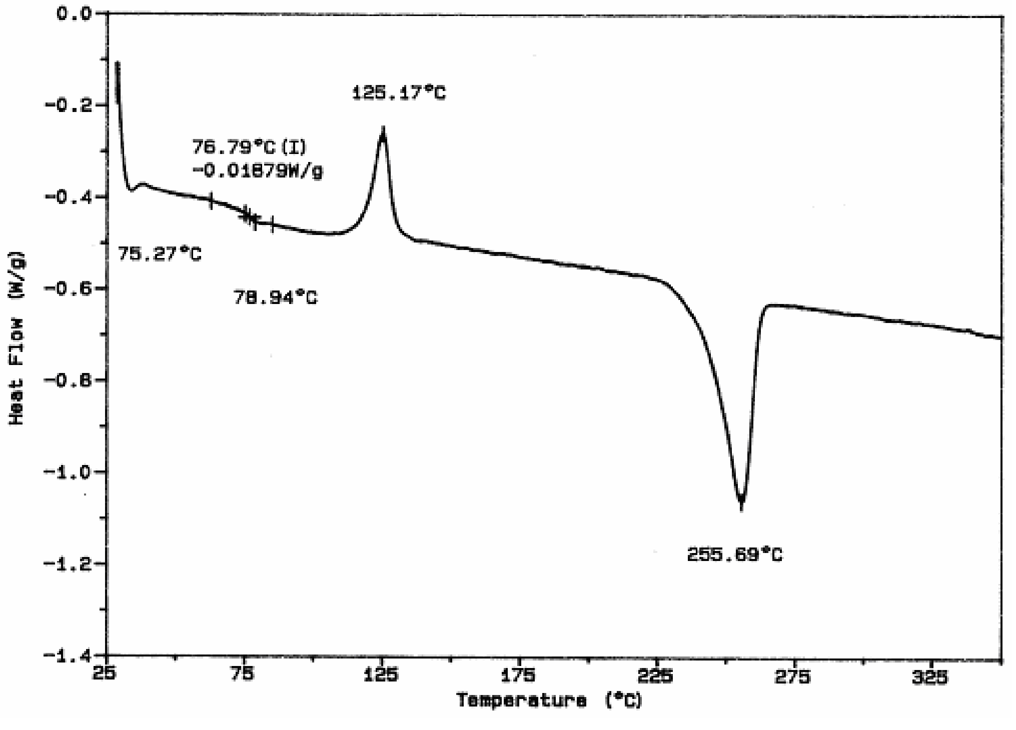


Figure 3.11 DSC Thermogram of PET-% 5 TLCP mixture

3.3 DMA INVESTIGATION OF PET-TLCP MIXTURES

The DMA spectra of PET, TLCP and PET-TLCP mixtures containing % 0.5, 2 and 5 TLCP are given in Figures 3.12 - 3.15.

The T_g of PET (Figure 3.6) is 60°C in DSC thermogram. However in DMA spectrum (Figure 3.12), the observed T_g 109°C. This is because of short range molecular sensitivity of DMA method. The T_g value of mixtures decrease considerably with the addition of TLCP (Figures 3.13-3.15). This value does not change much with the percentage of TLCP in the mixture. One T_g value in both DSC and DMA spectra of mixtures shows that PET and TLCP forms one phase matrix. However, the presence of TLCP even in small amounts changes T_g considerably due to interaction between PET and TLCP in molecular level.

The storage modulus (E'), loss modulus (E'') and tan δ values for PET and PET-TLCP mixtures are tabulated in Table 3.2. The storage modulus of PET decreased significantly with the addition of TLCP. However the change with percentage of added TLCP is not very large and there is a small increase with increase of TLCP percentage. This might be related to the type of the interaction of the two components that describe in introduction section. The loss modulus are not well defined in the spectra.

Table 3.2 DMA results for PET and PET-TLCP mixtures

	T_g (°C) (max tan δ)	E^{i} (GPa)	E^{ii} (MPa)
PET	109.0	2.75	119
PET - % 0.5 TLCP mixture	78.4	1.20	175
PET - % 2 TLCP mixture	79.6	1.43	-
PET - % 5 TLCP mixture	84.6	1.49	-

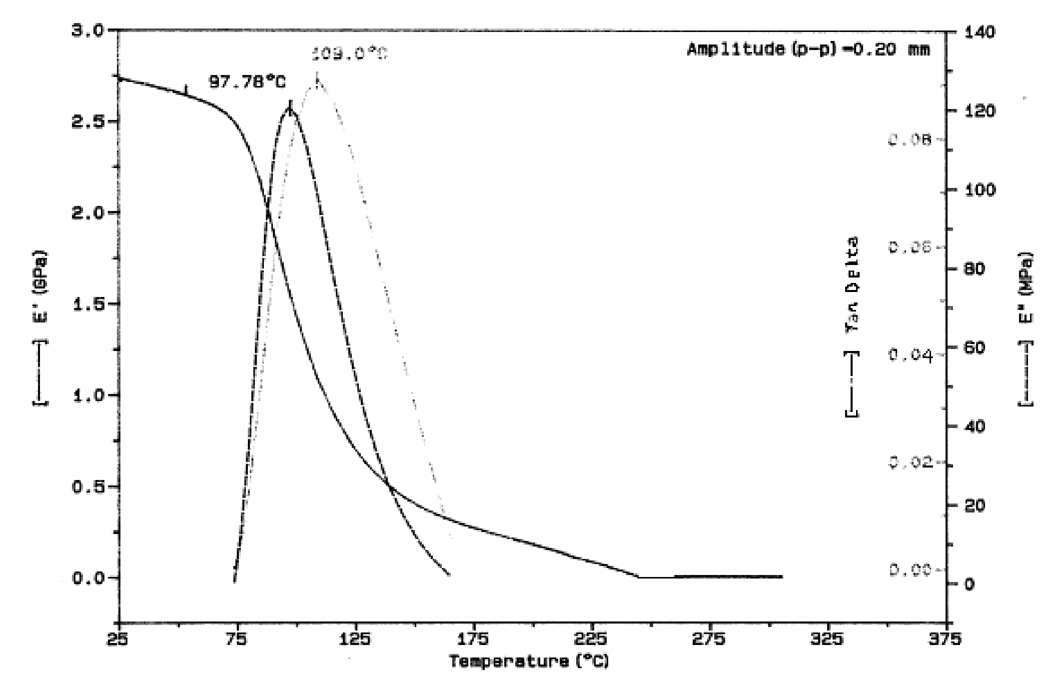


Figure 3.12 DMA Scan of PET

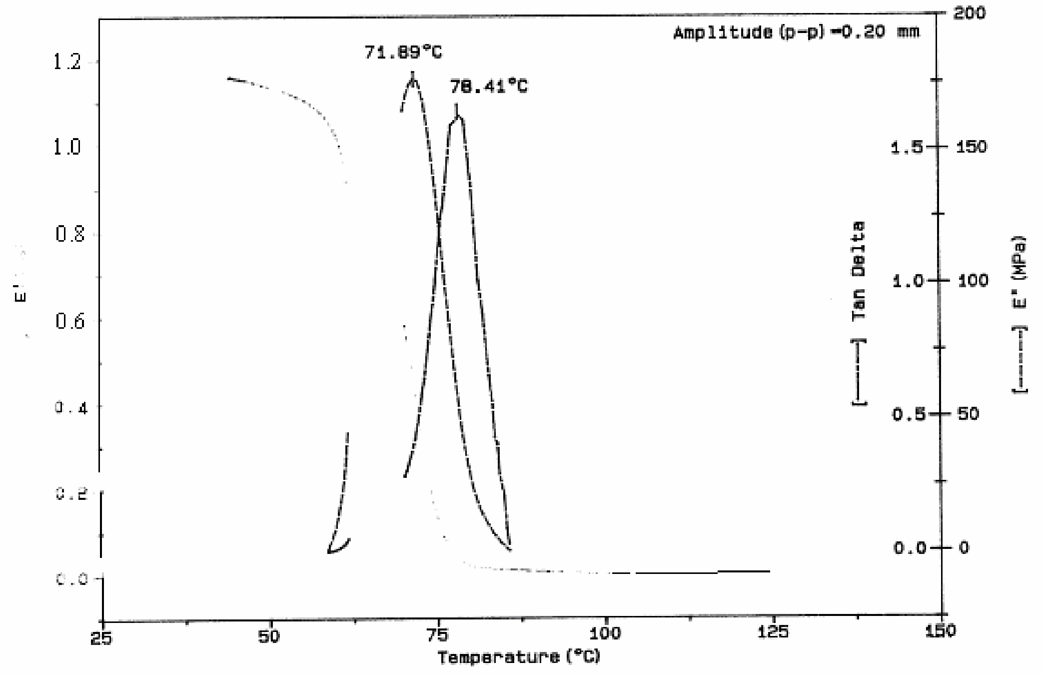


Figure 3.13 DMA Scan of PET-% 0.5 TLCP mixture

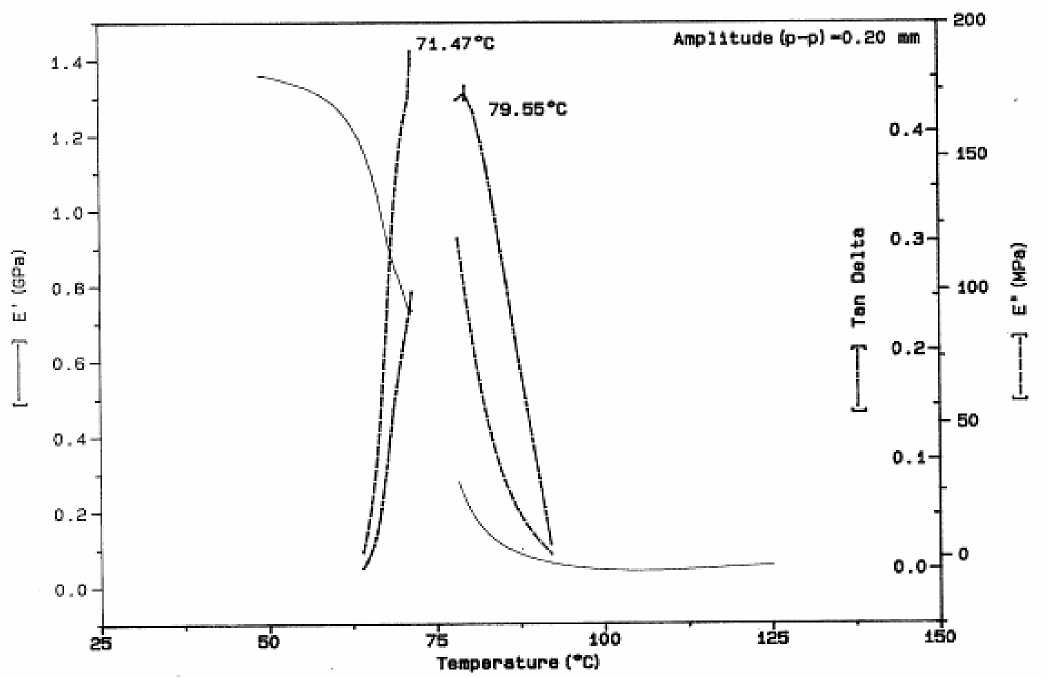


Figure 3.14 DMA Scan of PET- % 2 TLCP mixture

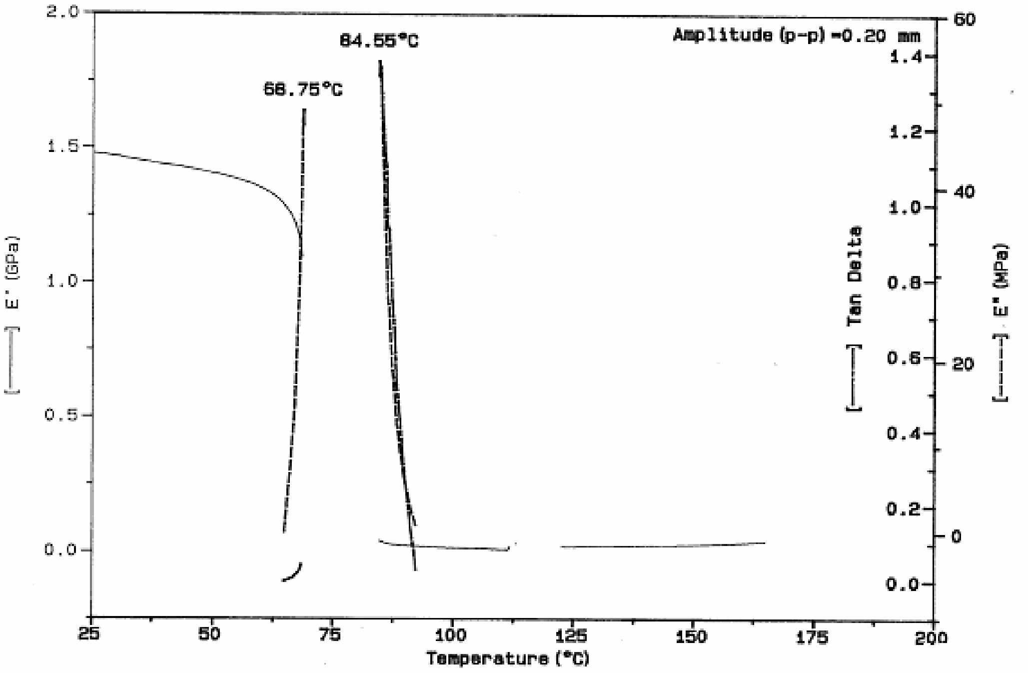


Figure 3.15 DMA Scan of PET- % 5 TLCP mixture

3.4 TENSILE TESTS OF PET-TLCP MIXTURES

The tensile curves of PET, TLCP and PET-TLCP mixtures containing % 0.5 – 2 – 5 TLCP are given in Figure 3.16 and the results are tabulated in Tables 3.3-3.6, respectively.

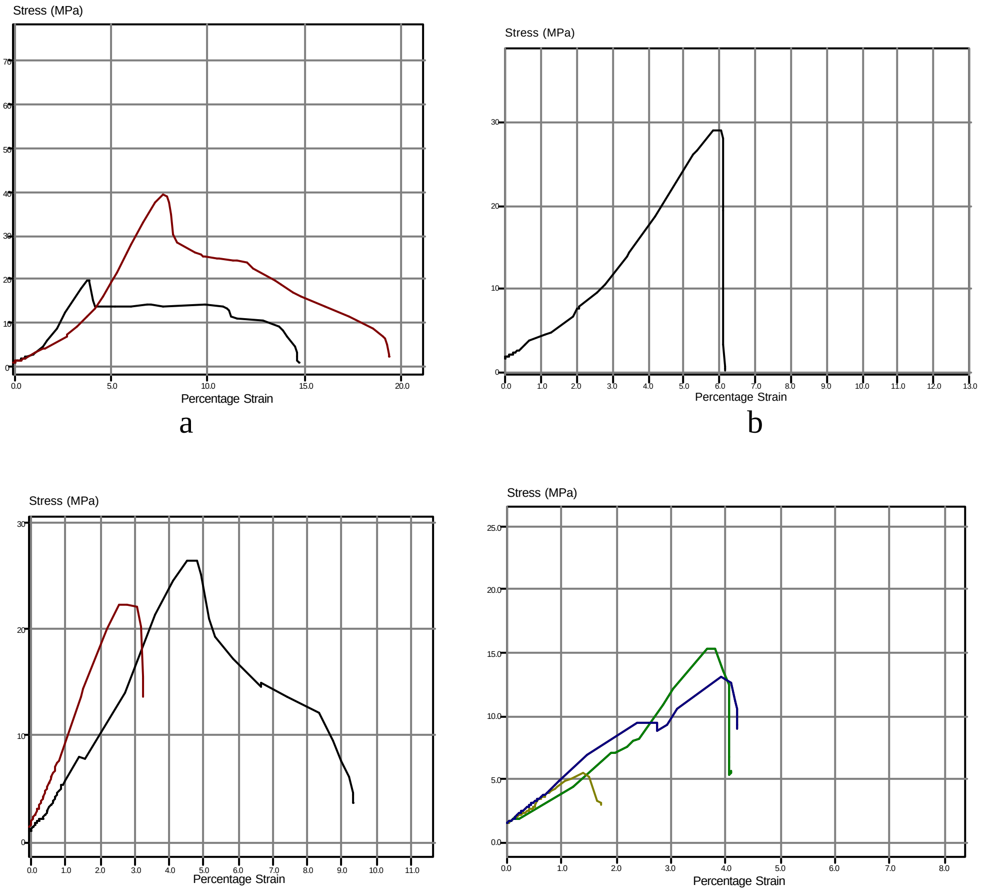
The measurement of impact and 3-point bending test samples were not accomplished because of the hard and brittle behaviour of mixtures.

Although PET has a ductile structure, because of the hard and brittle behaviour of TLCP, PET-TLCP mixtures also became hard and brittle even by the small additions of TLCP.

From tensile test results, it was shown that all values obtained from tensile tests were decreased by the addition of TLCP. The results are in the same trend as given for the DMA result however the first one is in the macro level where DMA gives interaction in molecular level. Therefore the differences are not compatible between two methods.

Table 3.3 Tensile Test Results of PET-TLCP mixtures

% TLCP	Stiffness (kN/m)		Tensile Strength (MPa)		Young's Modulus (MPa)		% Strain at break	
	MV	SD	MV	SD	MV	SD	MV	SD
PET	94	3	29.6	9.7	837	30	17	2
PET+% 0.5	53	2	28.8	0.4	717	32	10	4
PET+% 2	64	16	23	2.8	671	9	6	2
PET+% 5	56	0.4	14	1.1	653	5.6	4	0.07



a

b

c

d

Figure 3.16 The Stress-Strain curves of

a) PET
b) PET-% 0.5 TLCP mixture
c) PET-% 2 TLCP mixture
d) PET-% 5 TLCP mixture

3.5 FT-IR ANALYSIS OF PMMA REINFORCED WITH TLCP

The FT-IR spectrum obtained for 60 min heat cured PMMA is shown in Figure 3.17. The carbonyl peak is observed at 1731 cm^{-1}. The peaks at 1243-1147 cm^{-1} are due to the C-O-C (ether group). The aliphatic C-H stretching is observed at 2991 cm^{-1} and 747 cm^{-1}. The ester C-H stretching peak is observed at 2947 cm^{-1}. The peak at 986 cm^{-1} corresponds to the vinyl groups of residual monomer and/or chain end group due to the disproportionation of the termination. The sharpness of FT-IR peaks in polymer spectrum is also an evidence of some regularity of polymer structure.

The FT-IR spectra of all PMMA-TLCP mixtures are identical to that of PMMA. Since the amount of TLCP in PMMA is very small, the FT-IR peaks corresponding to TLCP molecules are not resolved in the spectrum.

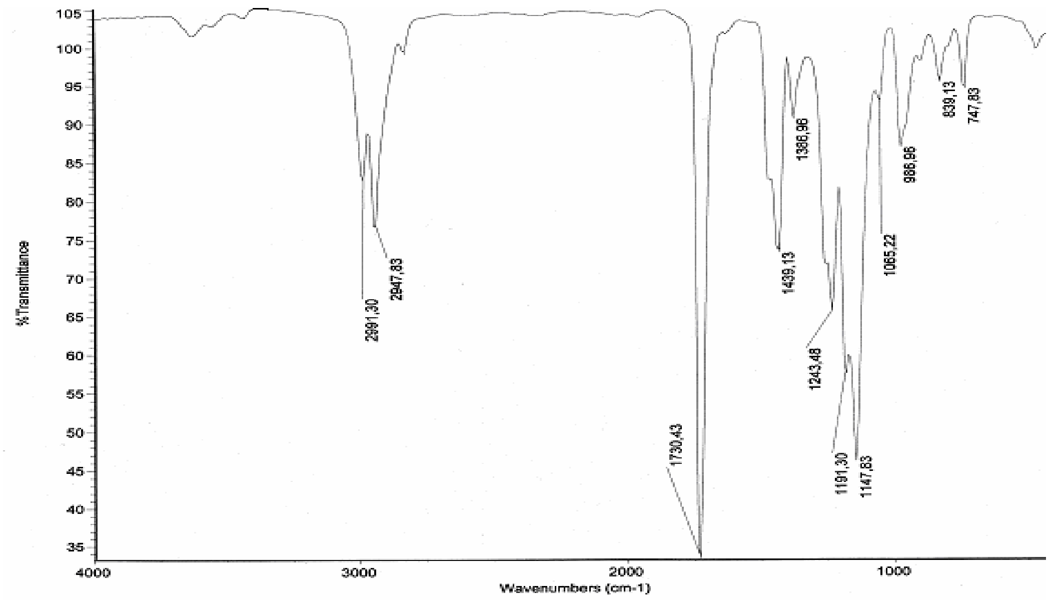
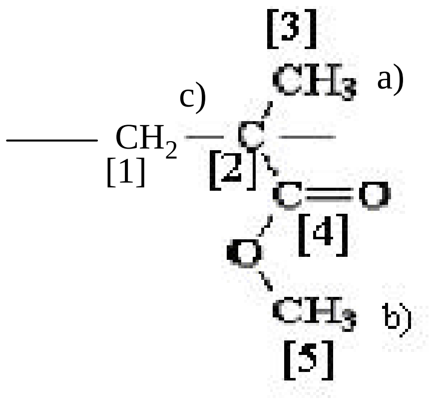


Figure 3.17 IR Spectra of 60 min heat cured PMMA

3.6 NMR ANALYSIS OF PMMA REINFORCED WITH TLCP

The ^{1}H-NMR spectrum of PMMA is given in Figure 3.18. The signals are assigned according to the given formula. The protons of methyl groups [peak a] of $-C(C\mathbf{H}_3)(COOCH_3)$ are at 0.59-0.95 ppm, methylene groups [peak c] of $C\mathbf{H}_2$ are at 1.17-1.77 ppm, and methoxy groups [peak b] $-C(CH_3)(COOC\mathbf{H}_3)$ are at 3.14-3.48 ppm. The peak at 4.6 ppm is assigned to the vinyl groups of methyl methacrylate. This peak shows termination by disproportionation as well as the presence of residual monomer. The peak at 7.2 ppm is assigned to the solvent, deutrated chloroform. The ^{1}H-NMR spectrum of PMMA reinforced with TLCP were identical for all compositions studied at this work. And they were also identical with that of pure PMMA. Therefore, no peak for TLCP were observed. This is because TLCP is not soluble in deutrated chloroform ($CDCl_3$).



The ^{13}C-NMR spectrum of PMMA is given in Figure 3.19. The signals are assigned according to the given formula: carbon [3] at 16.52-18.71 ppm, carbon [1] at 44.6-44.89, carbon [2] at 51.8-54.4 ppm, carbon [5] at 77.7-77.3 ppm and carbon [4] at 177-178 ppm. The ^{13}C-NMR spectrum of PMMA reinforced with TLCP were identical for all compositions studied at this work. And they were also identical with that of pure PMMA. Therefore, no peak for TLCP were observed. This is because TLCP is not soluble in $CDCl_3$.

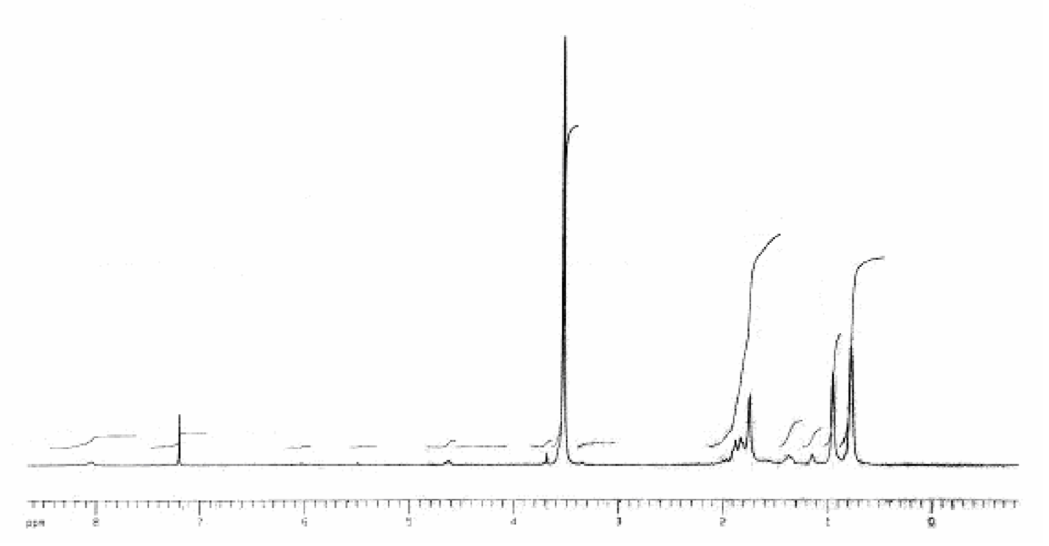


Figure 3.18 ^{1}H-NMR of heat cured PMMA

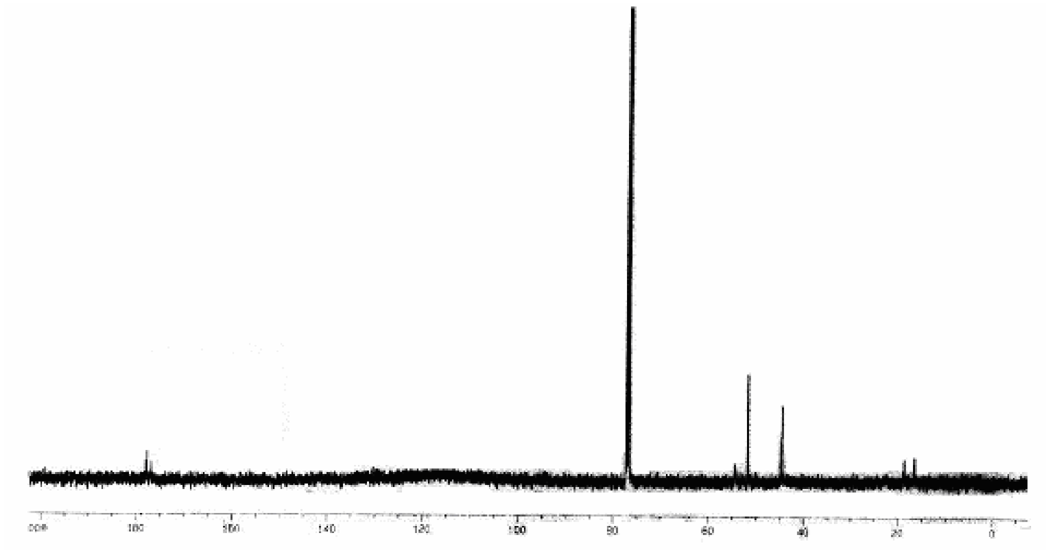


Figure 3.19 ^{13}C-NMR of heat cured PMMA

3.7 DSC ANALYSIS OF PMMA REINFORCED WITH TLCP

The DSC thermograms of 60 min heat cured PMMA, 90 min and 8 day gamma cured PMMA, 2 min microwave cured PMMA are given in Figures 3.20-3.23. The results are also tabulated in Table 3.4. The T_g of the 60 min heat cured PMMA (Figure 3.20) is 120°C and no crosslinking peak was observed. The T_g for gamma cured sample is not observed when irradiated 90 min, but it is 119°C for irradiation of 8 days. The crosslinking peak (100-150°C range) covers the peak expected for the T_g in 90 min irradiated sample. There is no crosslinking peak in the spectrum of 8 days irradiated sample. For 2-min microwave cured sample also a crosslinking peak (105-140°C range) covers the T_g peak. The crosslinking peak shows that curing is not completed under the given conditions.

Table 3.4 DSC results of heat, gamma and microwave cured PMMA

PMMA cured by	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C)
60 min Heat	120	-	-	-
90 min Gamma	-	120	-	-
8 day Gamma	119	-	-	-
2 min Microwave	-	121	-	-

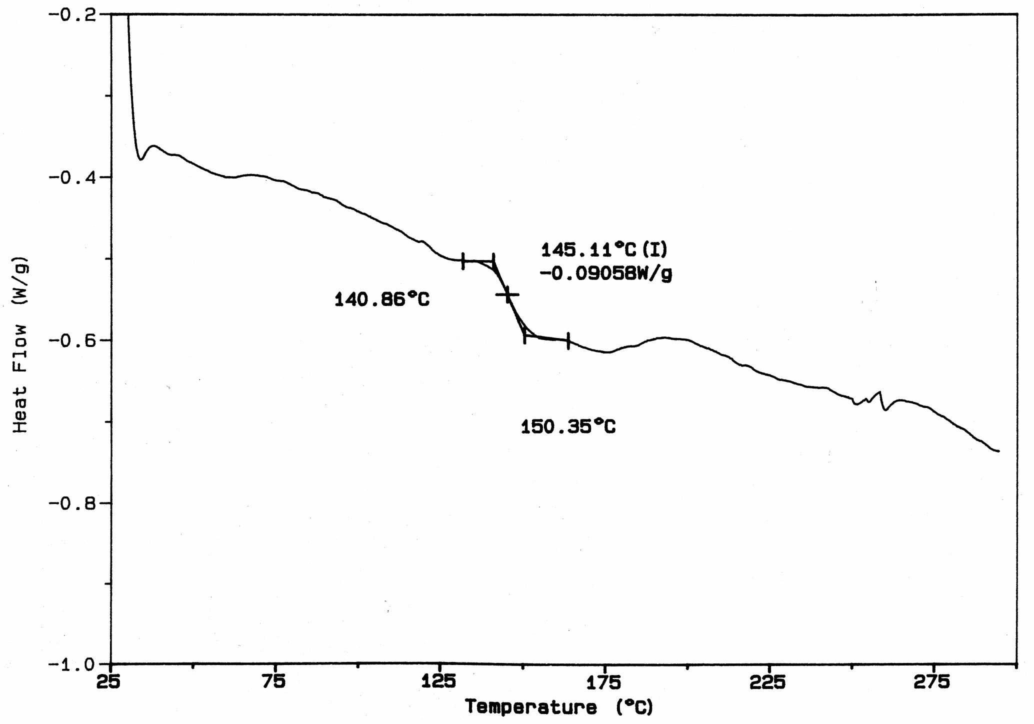


Figure 3.20 DSC Thermogram of 60 min heat cured PMMA

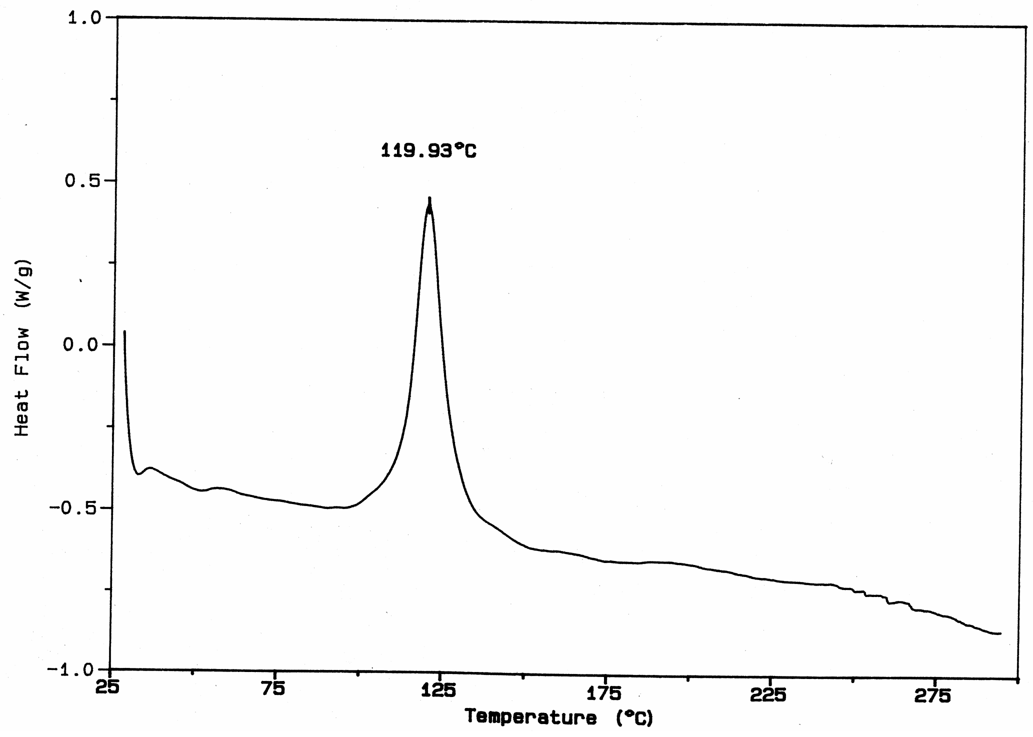


Figure 3.21 DSC Thermogram of 90 min gamma cured PMMA

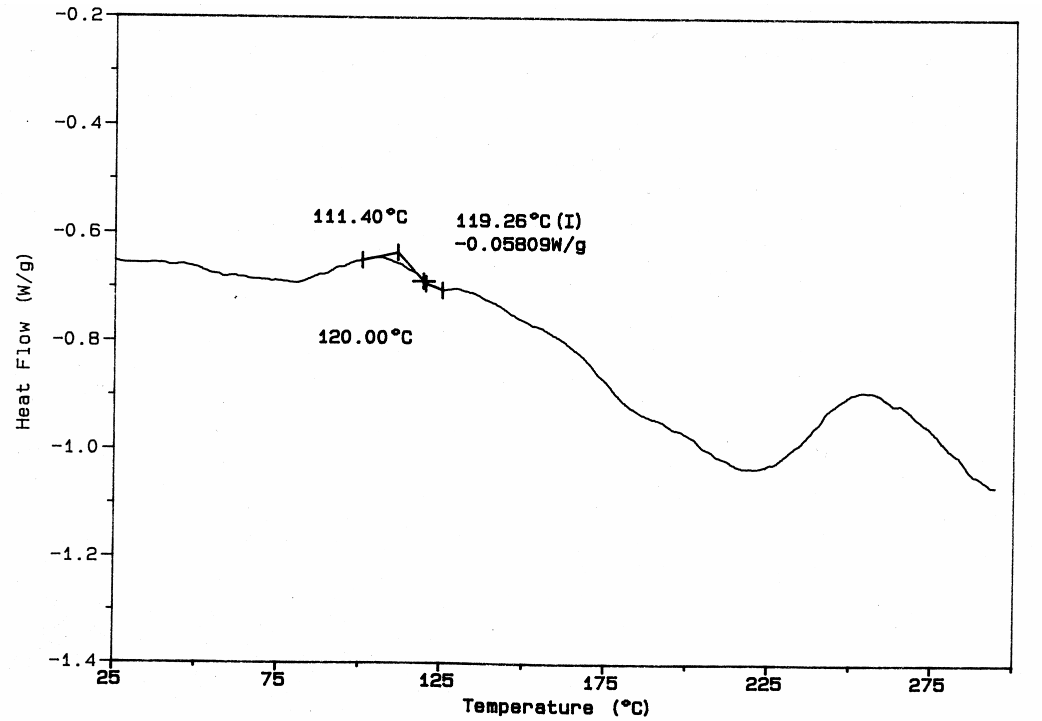


Figure 3.22 DSC Thermogram of 8 day gamma cured PMMA

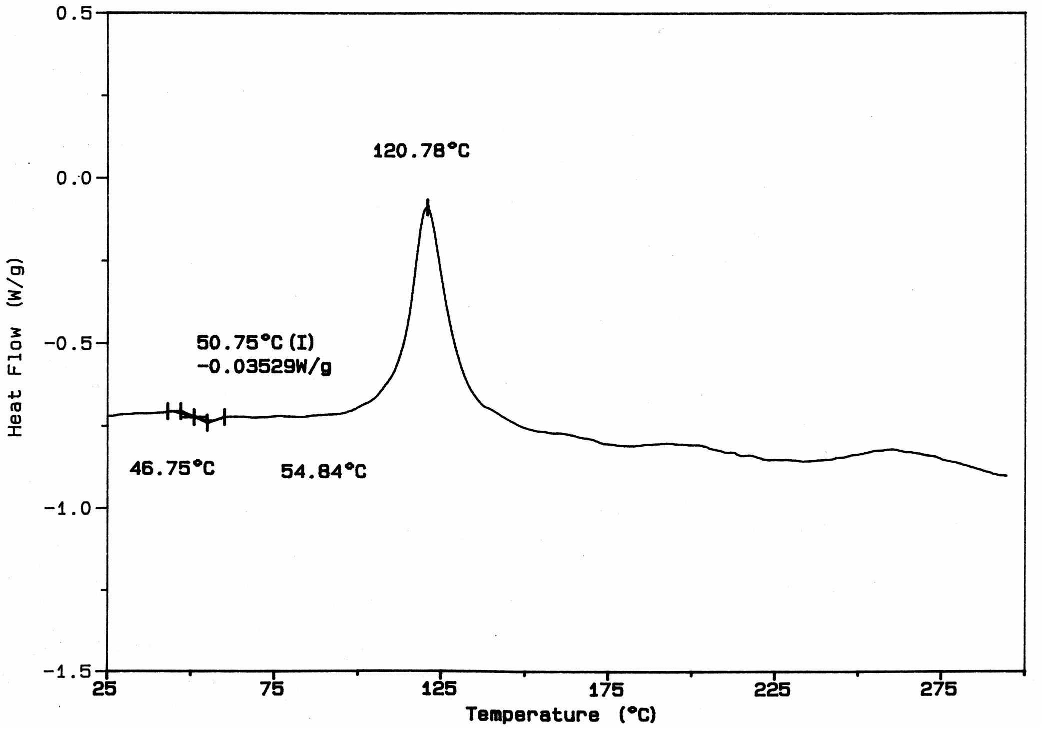


Figure 3.23 DSC Thermogram of 2 min microwave cured PMMA

3.8 DMA INVESTIGATION OF PMMA REINFORCED WITH TLCP

The DMA spectra for heat, gamma and microwave cured PMMA-TLCP mixtures containing % 0.5 – 2 – 5 and silane treated % 0.5 TLCP are given in Figures 3.24- 3.46 and the results are tabulated in Tables 3.5-3.7.

The T_g value for 60-min heat cured unreinforced PMMA is 131°C (Table 3.5) and that of reinforced with TLCP shows small differences. The changes are not statistically significant. The storage modulus (E') are increased for the reinforced samples. Even though the increase are statistically significant, there is no regular trend of change with concentration of TLCP. However for silane coupled sample, E' is increased more. Similar trends are also observed for loss modulus (E'').

For 30 and 90 min. gamma cured PMMA samples T_g is about 68°C whereas 8-day gamma cured samples T_g is about 120°C. This shows that the average overall molecular weight is much lower for 30 and 90-min gamma irradiation, the curing is incomplete. The change of T_g with reinforcing agent is not statistically significant. There is a significant decrease in storage modulus with additon of TLCP but the change is not following a regular trend with the concentration of additive. The loss modulus were decreased with addition of TLCP. However the amount of decrease is not related to the concentration of TLCP. These show that the distribution of TLCP in PMMA is not in a regular order in molecular level as was observed in the case of PET. This behaviour is also supported by optical photographs given in the later sections.

For the microwave cured samples (Table 3.7), the T_g value is closer to that of 8-day gamma cured samples however smaller than the values for heat curing. This is because the sudden temperature increase in the matrix of the sample causes evaporation of rest monomers which produces voids in sample. The result is lower crosslinking level and poorer mechanical strength. The smaller storage modulus for these samples is also the result of this behaviour.

Table 3.5 DMA results for heat cured PMMA-TLCP mixtures

HEAT-CURED	T_g (°C)	E^i (GPa)	E^{ii} (MPa)
PMMA	131	1.9	160
PMMA-% 0,5 TLCP	130	2.5	180
PMMA-% 0,5 TLCP-Silane	125	3.3	260
PMMA-% 2 TLCP	130	2.6	180
PMMA-% 5 TLCP	125	2.5	163

Table 3.6 DMA results for gamma cured PMMA-TLCP mixtures

GAMMA-CURED	T_g (°C)	E^i (GPa)	E^{ii} (MPa)
PMMA (30 min)	68.3	1.5	215
PMMA-% 0,5 TLCP (30 min)	69.8	0.56	75
PMMA-% 0,5 TLCP –Silane (30 min)	69.97	0.86	133
PMMA-% 2 TLCP (30 min)	71.2	1.3	190
PMMA-% 5 TLCP (30 min)	67.9	1.08	185
PMMA (90 min)	68.3	1.15	195
PMMA-% 0,5 TLCP (90 min)	66.3	0.75	135
PMMA-% 0,5 TLCP –Silane (90 min)	67.9	1.1	175
PMMA-% 2 TLCP (90 min)	70.8	1.15	245
PMMA-% 5 TLCP (90 min)	71.99	0.86	103
PMMA (8 day)	120.2	1.91	155
PMMA-% 0,5 TLCP (8 day)	123.4	1.1	110.4
PMMA-% 0,5 TLCP –Silane (8 day)	117.4	0.77	76

Table 3.7 DMA results for microwave cured PMMA-TLCP mixtures

MICROWAVE-CURED	T_g (°C)	E^{i} (GPa)	E^{ii} (MPa)
PMMA	123	1.2	90
PMMA-% 0,5 TLCP	121.8	1.80	177
PMMA- % 0,5 TLCP - silane	107.2	1.63	173
PMMA-% 2 TLCP	121.4	1.1	150
PMMA-% 5 TLCP	117.8	1.7	177

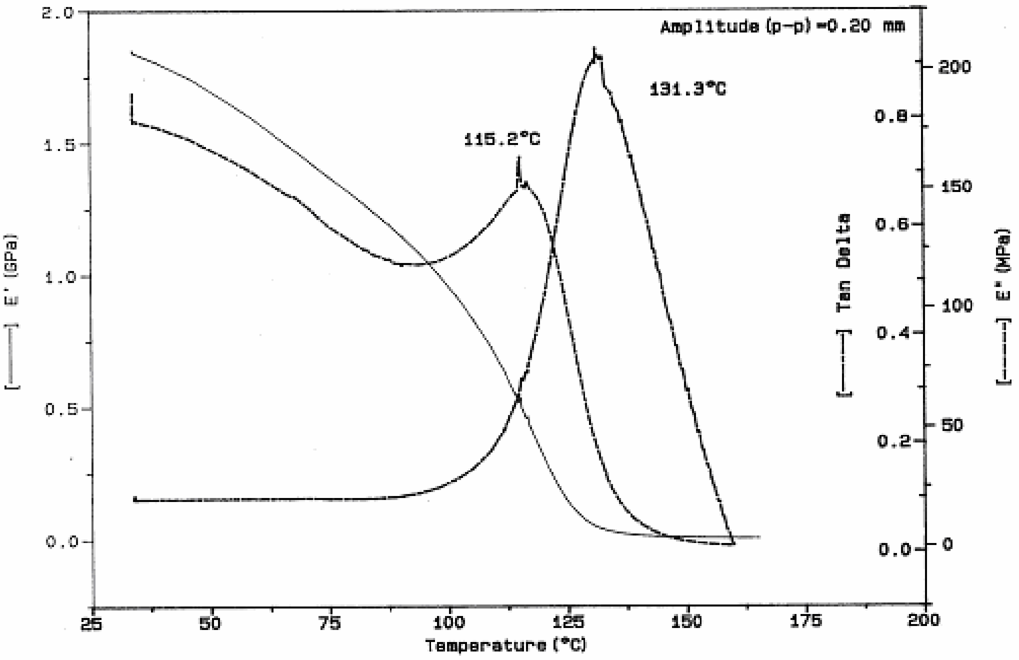


Figure 3.24 DMA Scan of 60 min heat cured PMMA

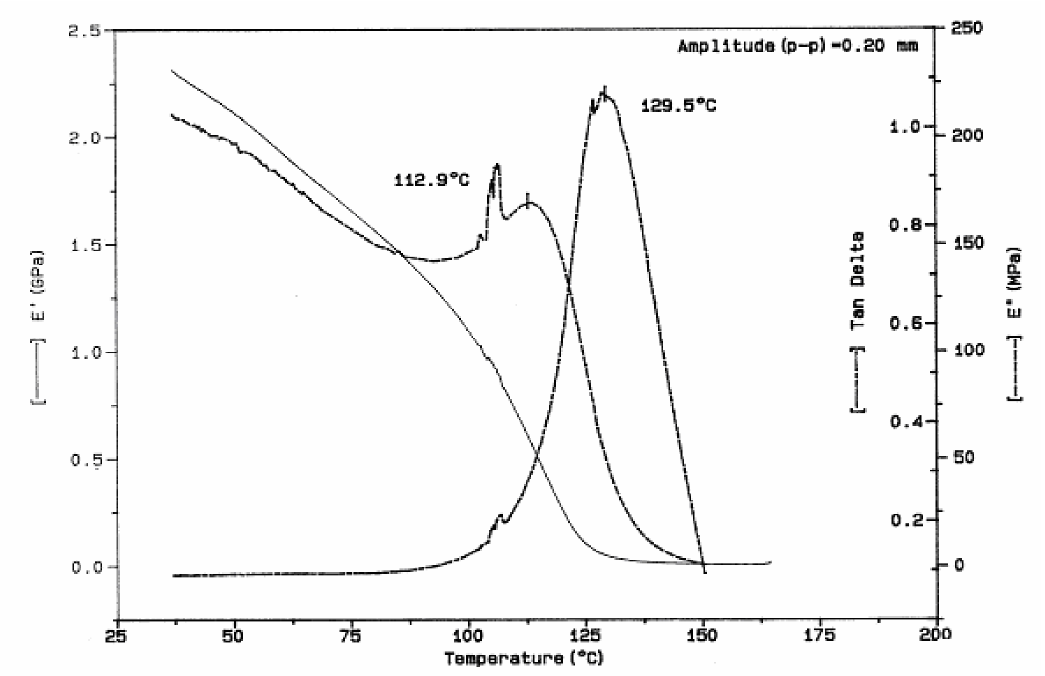


Figure 3.25 DMA Scan of 60 min heat cured PMMA-% 0.5 TLCP mixture

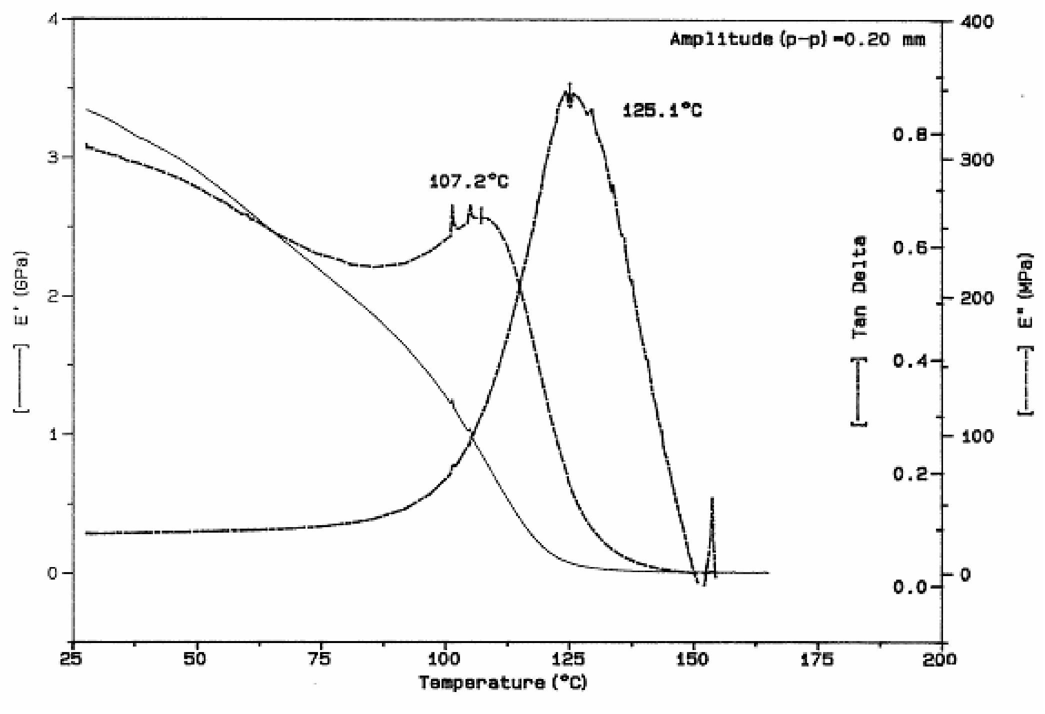


Figure 3.26 DMA Scan of 60 min heat cured PMMA-silane treated % 0.5 TLCP mixture

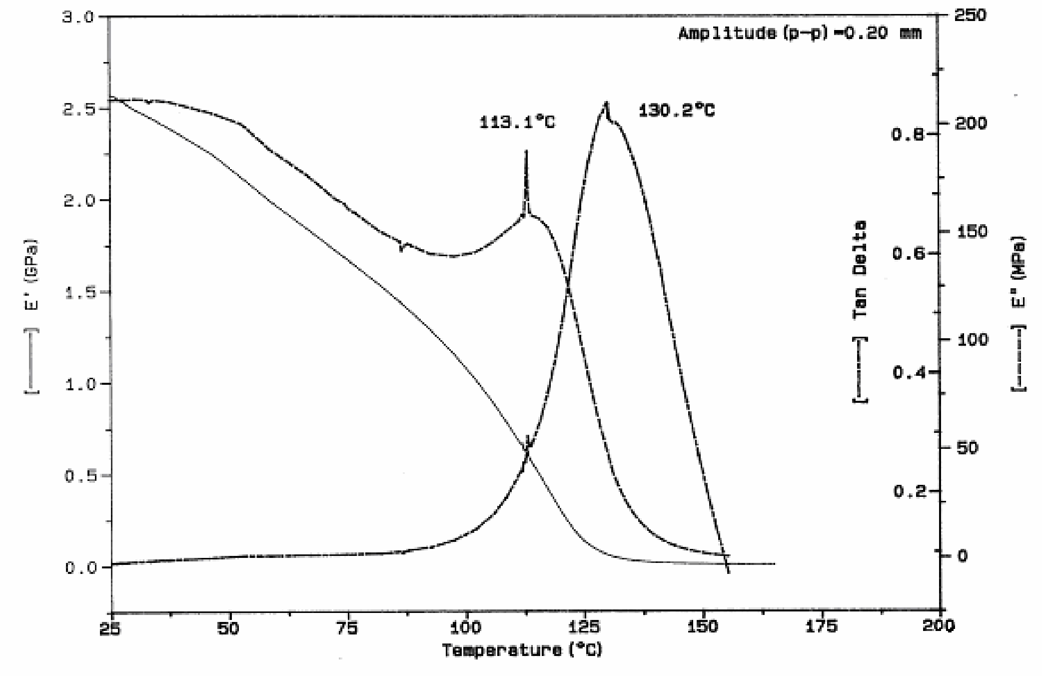


Figure 3.27 DMA Scan of 60 min heat cured PMMA- % 2 TLCP mixture

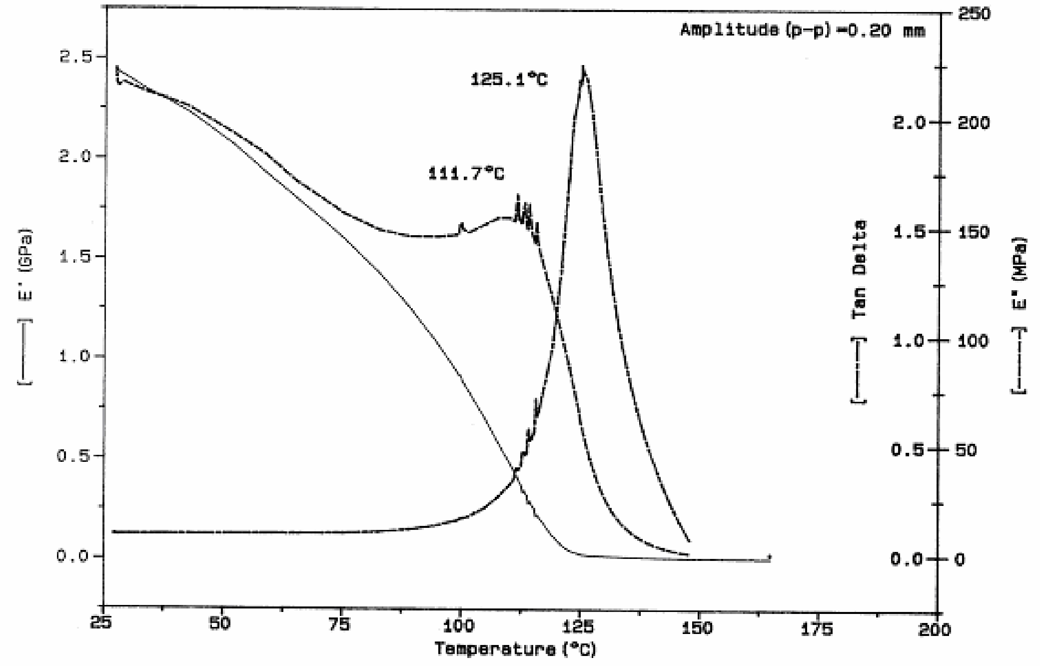


Figure 3.28 DMA Scan of 60 min heat cured PMMA- % 5 TLCP mixture

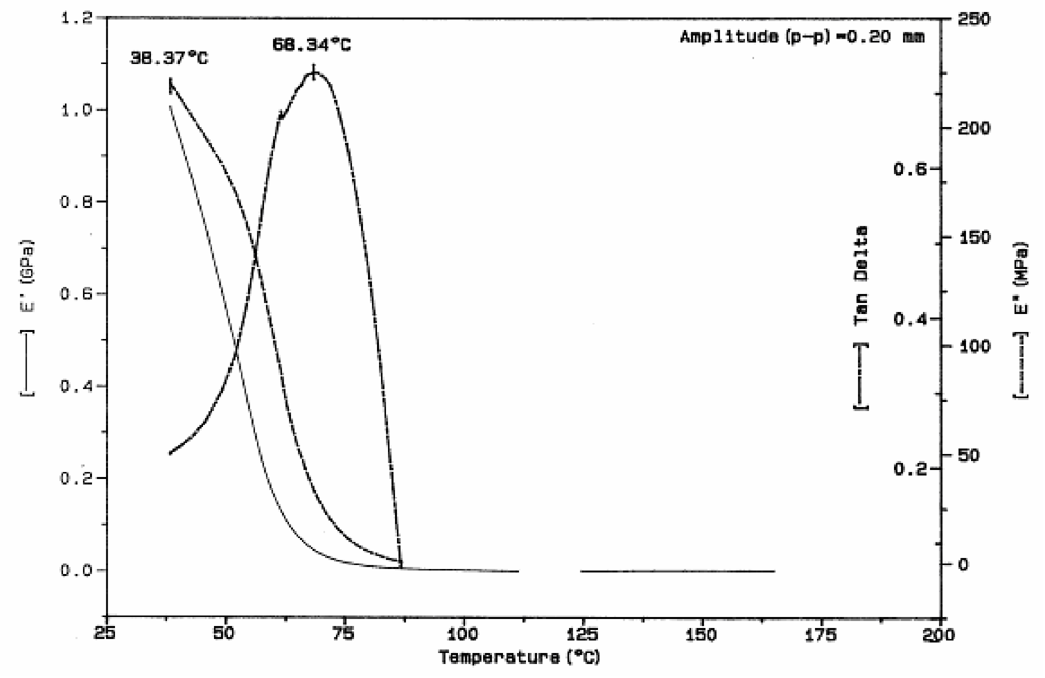


Figure 3.29 DMA Scan of 30 min gamma cured PMMA

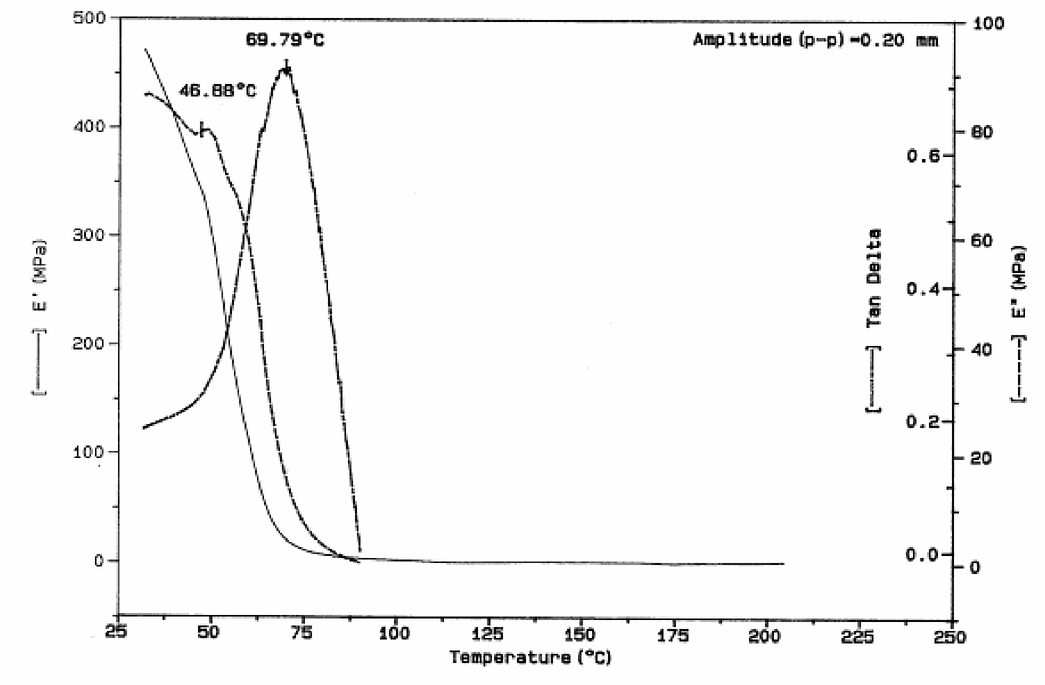


Figure 3.30 DMA Scan of 30 min gamma cured PMMA-% 0.5 TLCP mixture

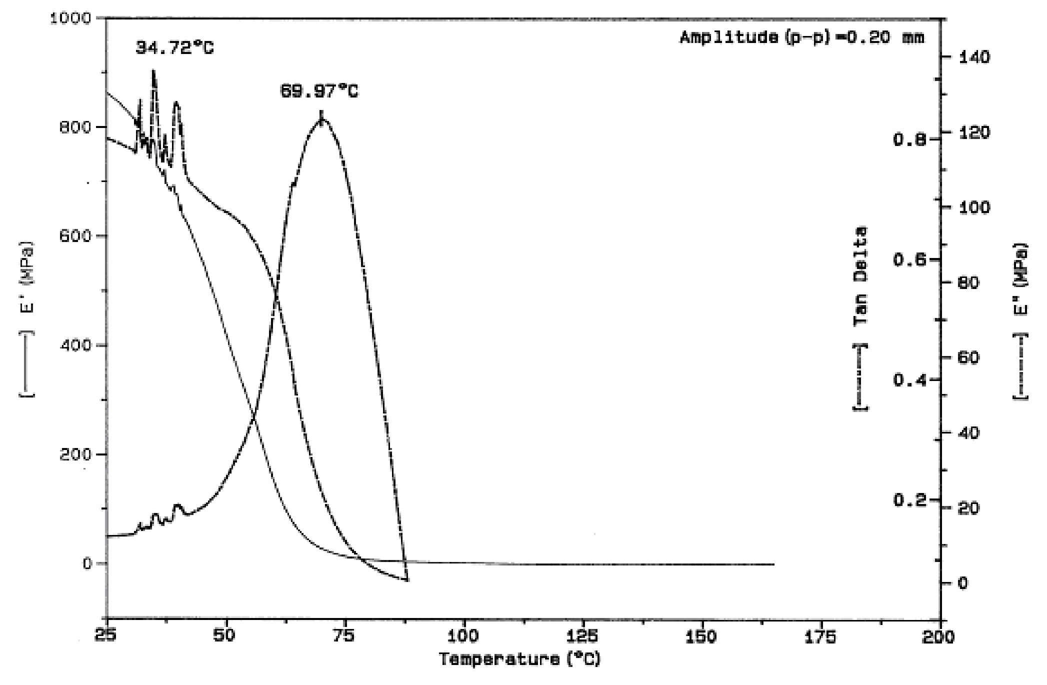


Figure 3.31 DMA Scan of 30 min gamma cured PMMA-silane treated % 0.5 TLCP mixture

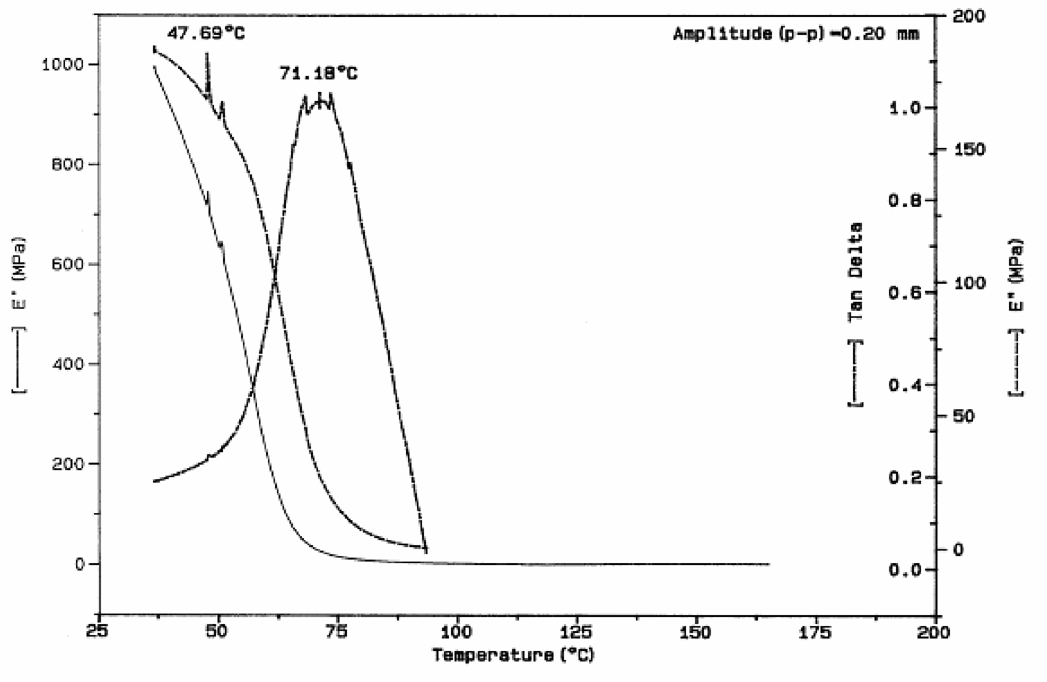


Figure 3.32 DMA Scan of 30 min gamma cured PMMA-% 2 TLCP mixture

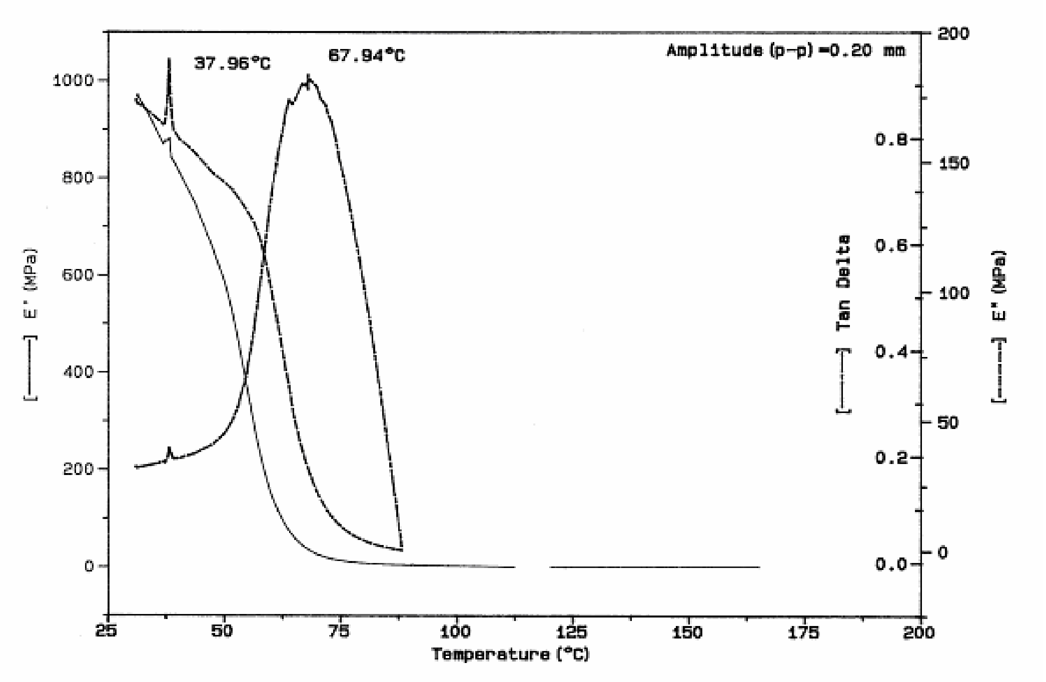


Figure 3.33 DMA Scan of 30 min gamma cured PMMA-% 5 TLCP mixture

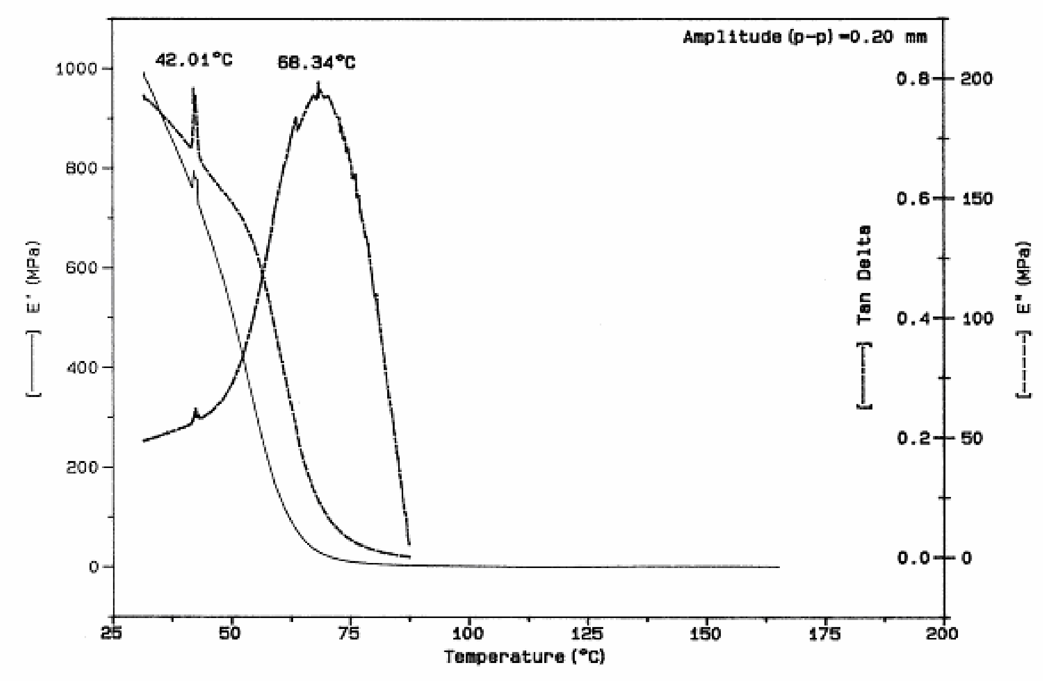


Figure 3.34 DMA Scan of 90 min gamma cured PMMA

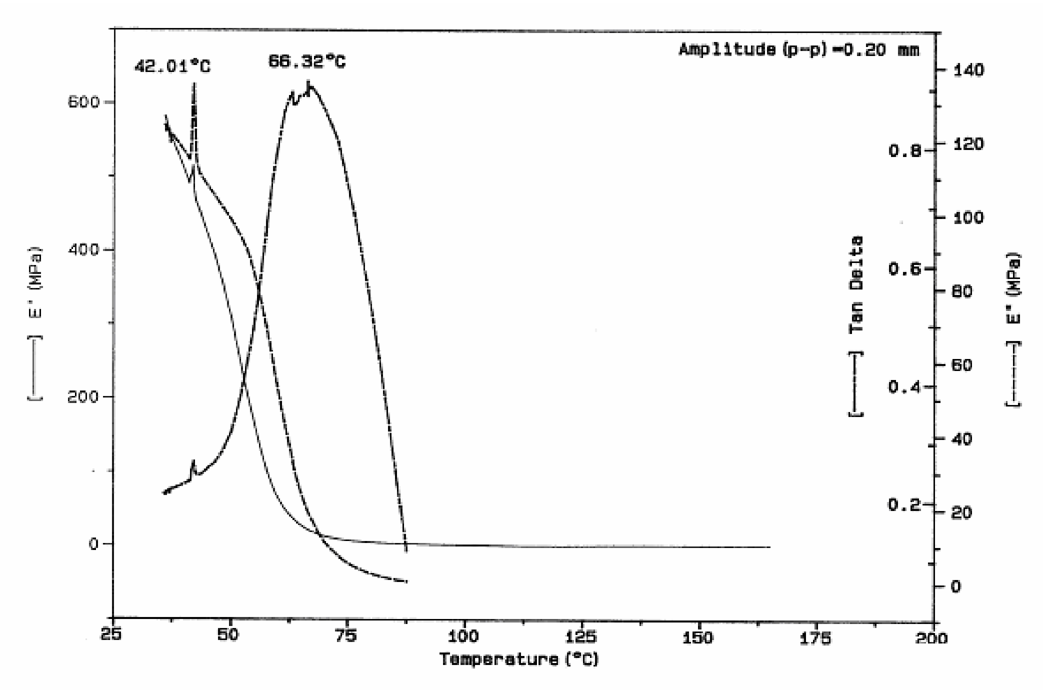


Figure 3.35 DMA Scan of 90 min gamma cured PMMA-% 0.5 TLCP mixture

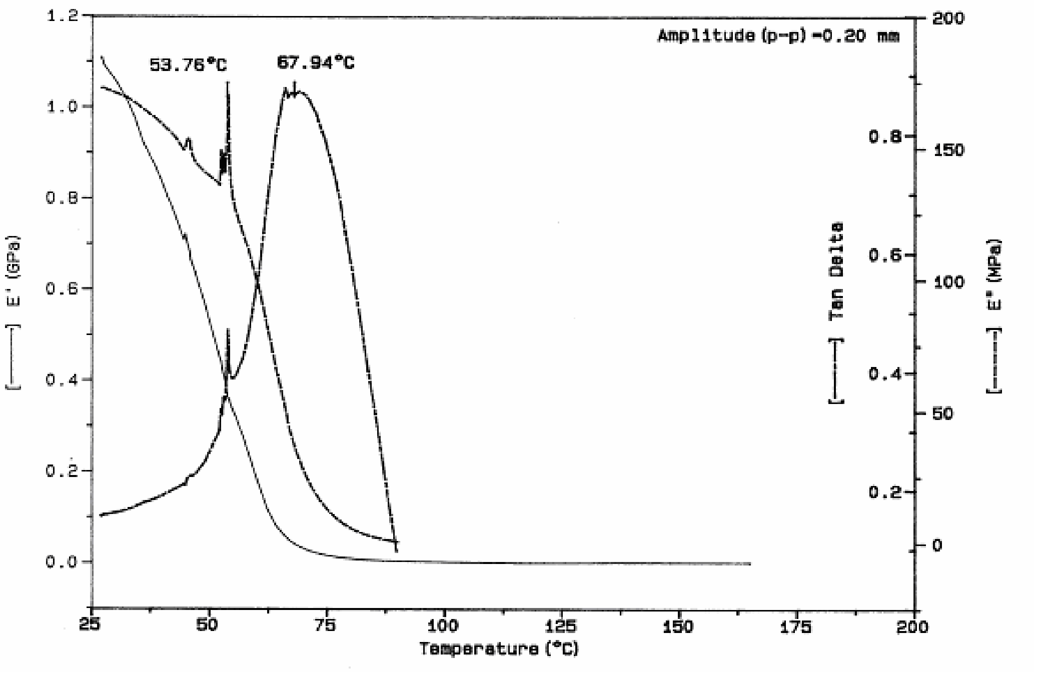


Figure 3.36 DMA Scan of 90 min gamma cured PMMA-silane treated % 0.5 TLCP mixture

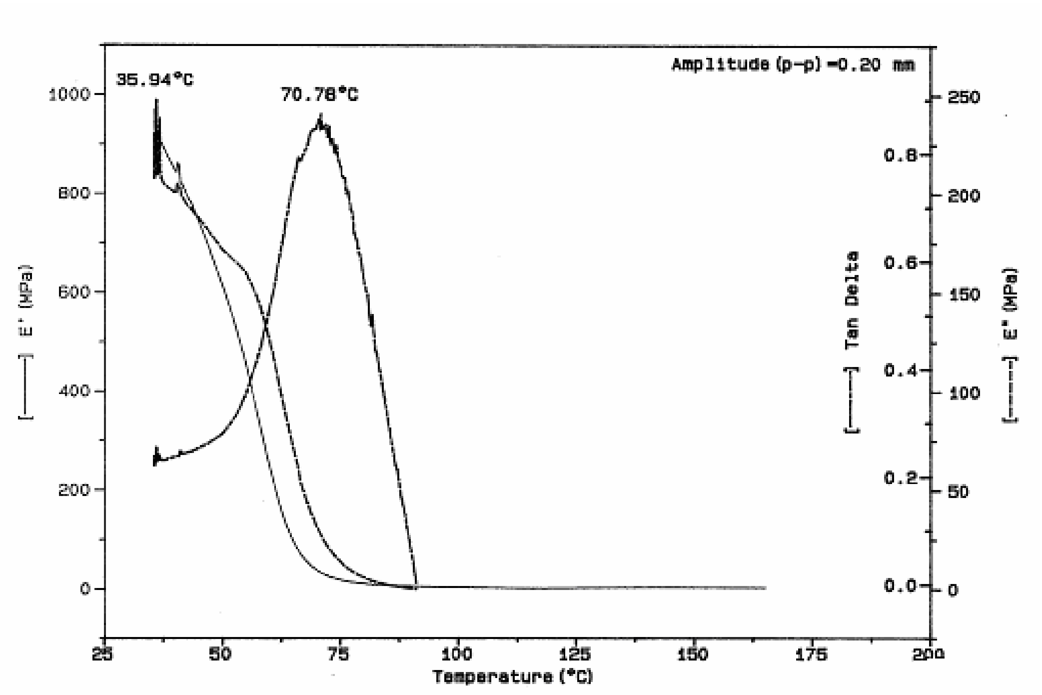


Figure 3.37 DMA Scan of 90 min gamma cured PMMA- % 2 TLCP mixture

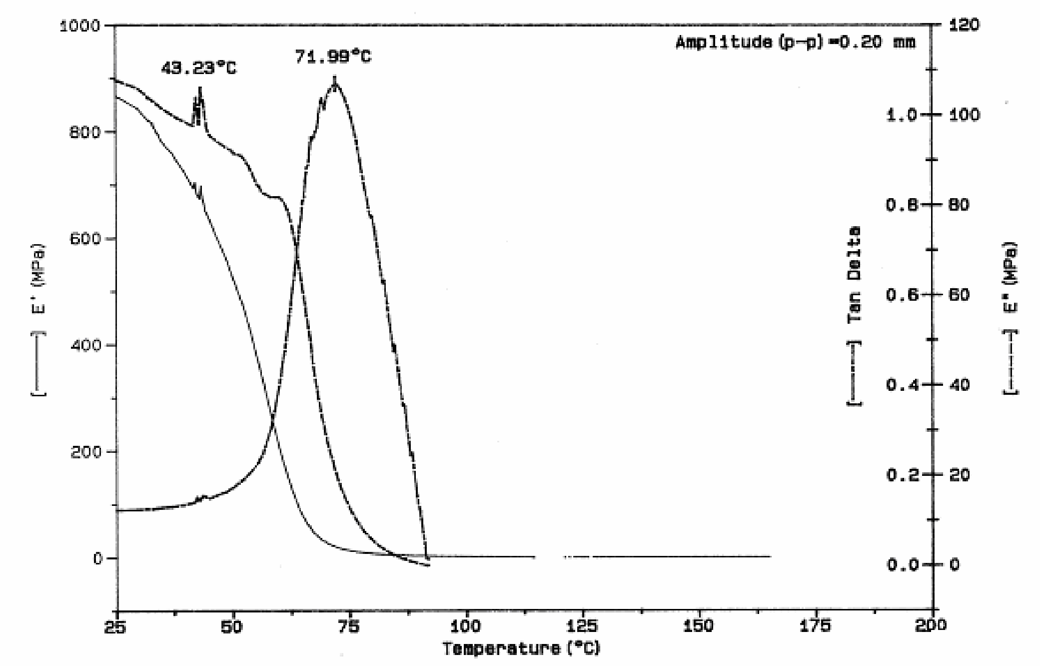


Figure 3.38 DMA Scan of 90 min gamma cured PMMA- % 5 TLCP mixture

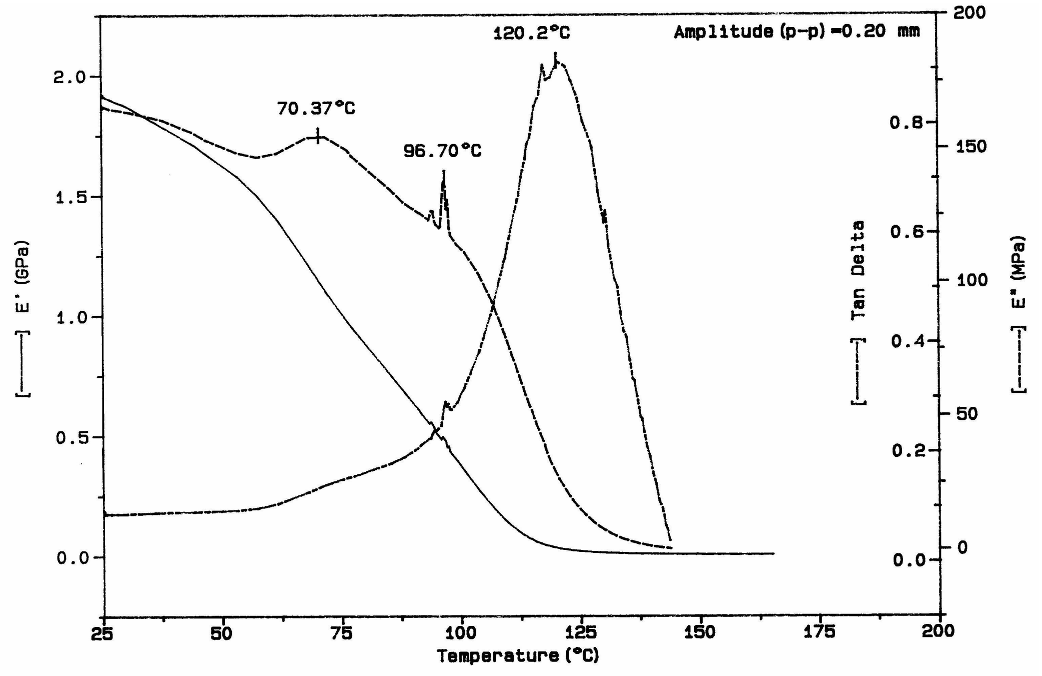


Figure 3.39 DMA Scan of 8 day gamma cured PMMA

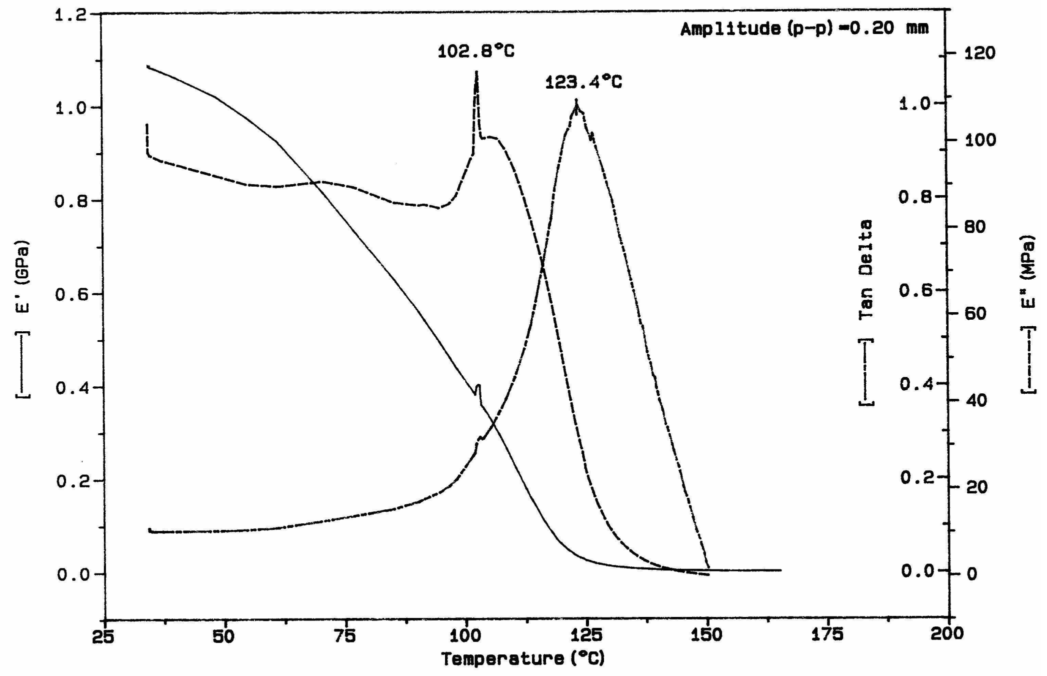


Figure 3.40 DMA Scan of 8 day gamma cured PMMA-% 0.5 TLCP mixture

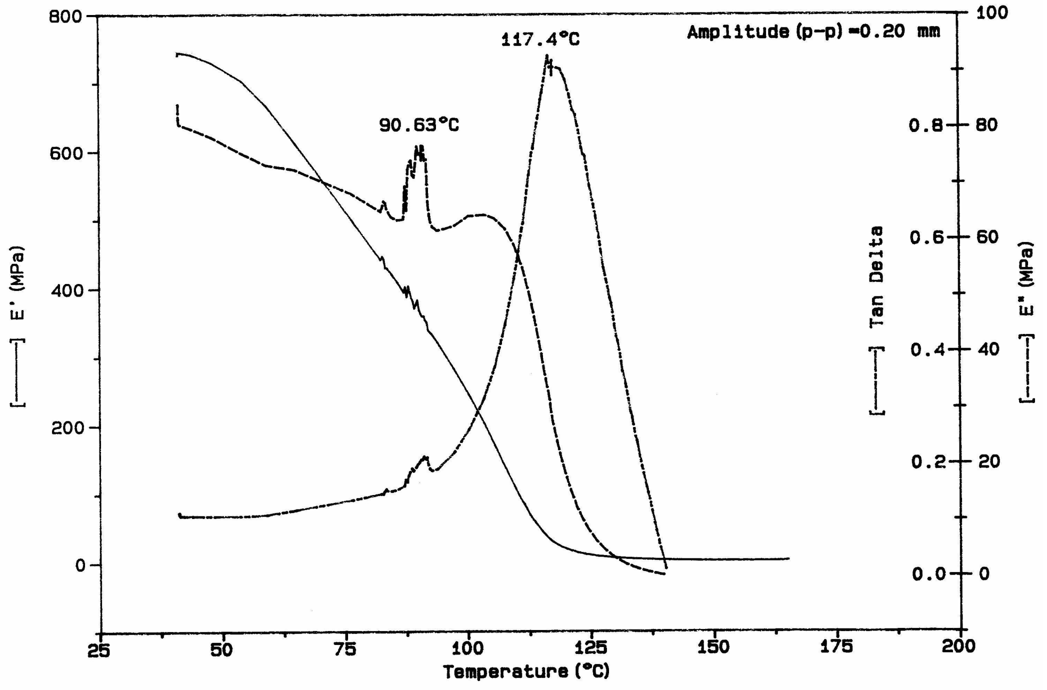


Figure 3.41 DMA Scan of 8 day gamma cured PMMA-silane treated % 0.5 TLCP mixture

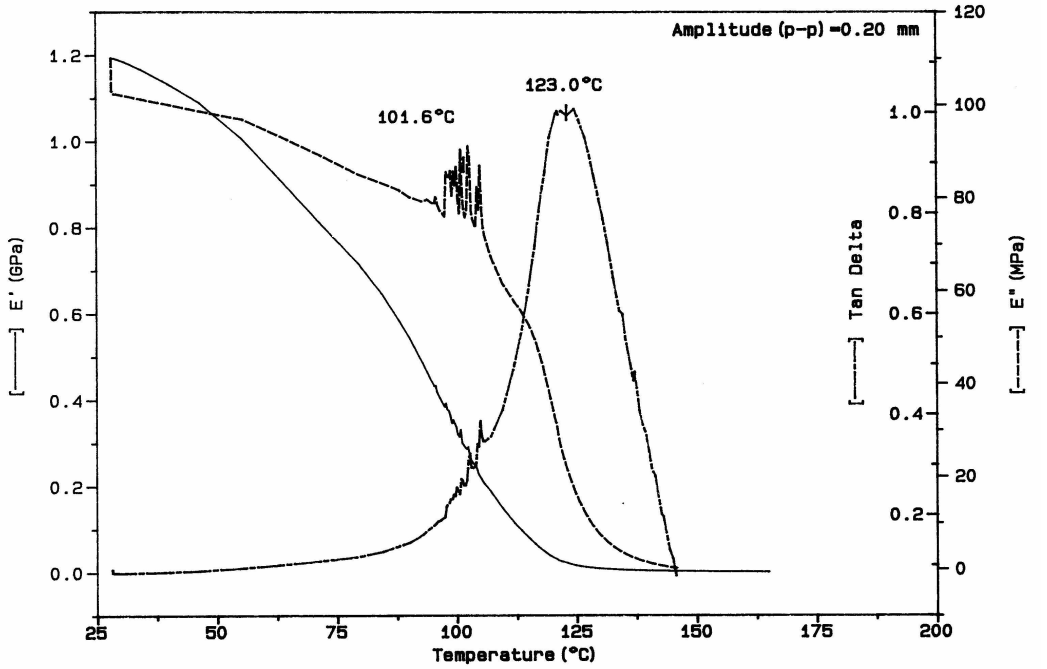


Figure 3.42 DMA Scan of 2 min microwave PMMA

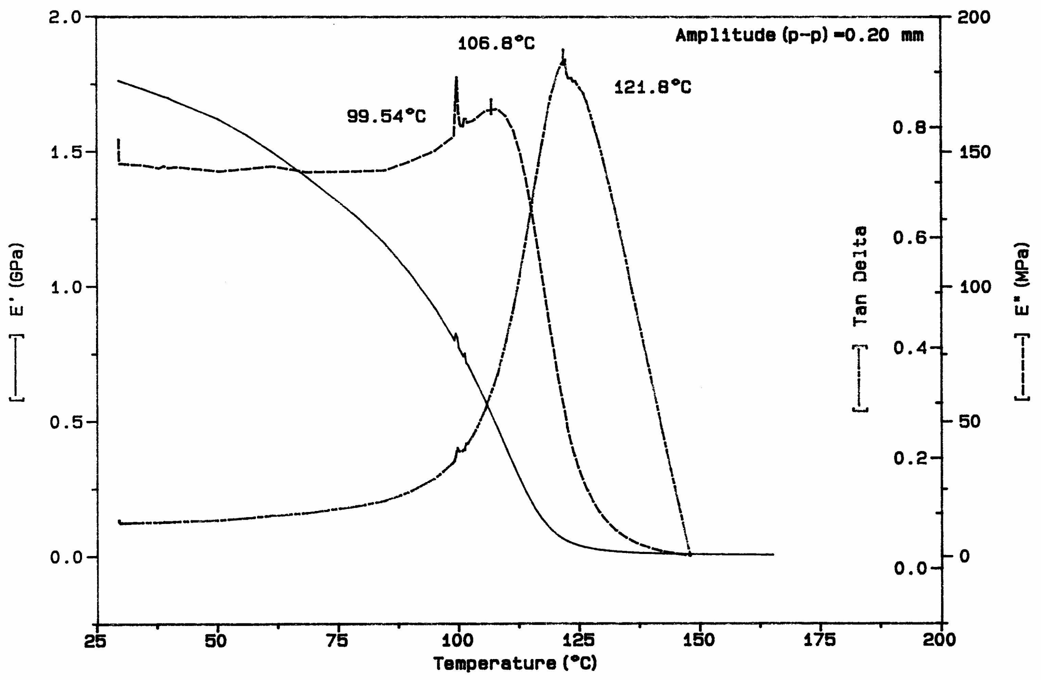


Figure 3.43 DMA Scan of 2 min microwave PMMA-% 0.5 TLCP mixture

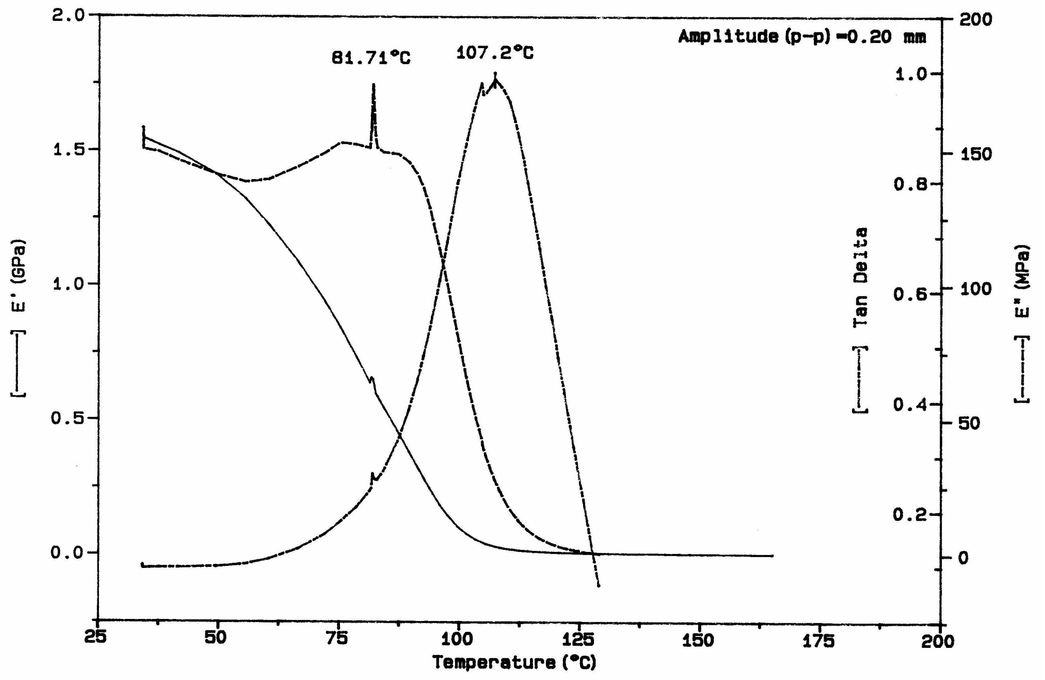


Figure 3.44 DMA Scan of 2 min microwave PMMA-silane treated % 0.5 TLCP mixture

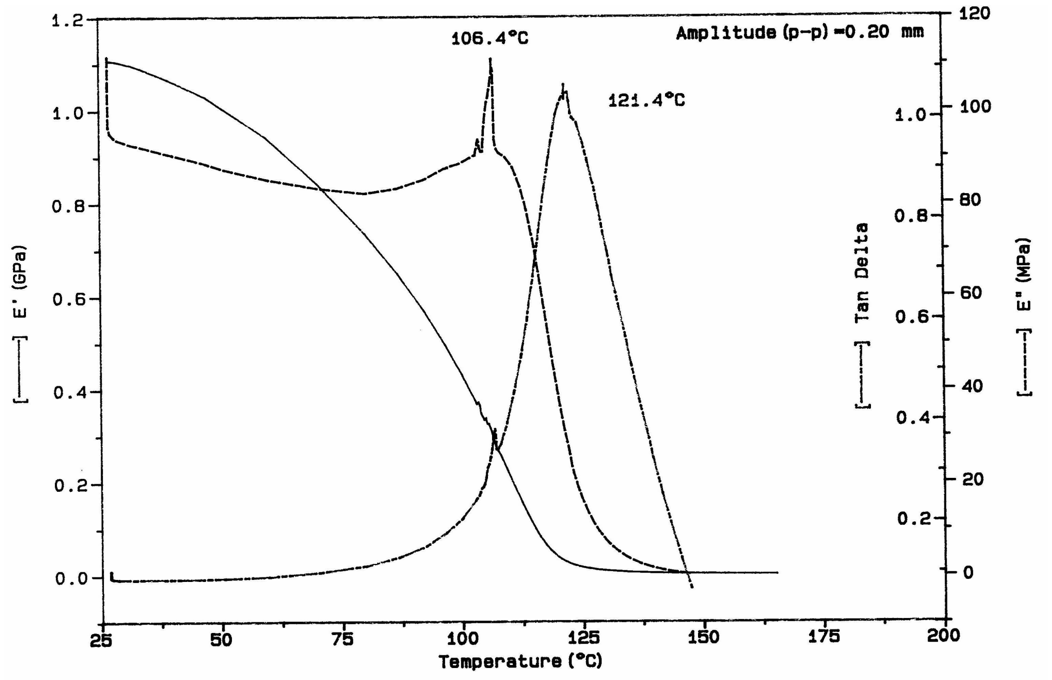


Figure 3.45 DMA Scan of 2 min microwave PMMA- % 2 TLCP mixture

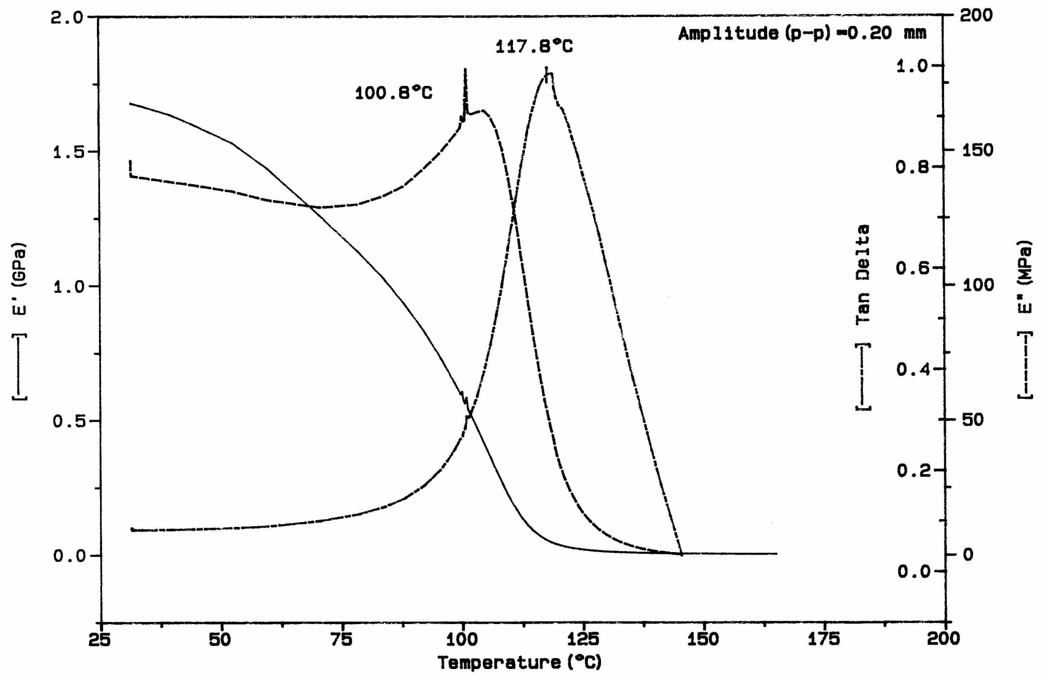
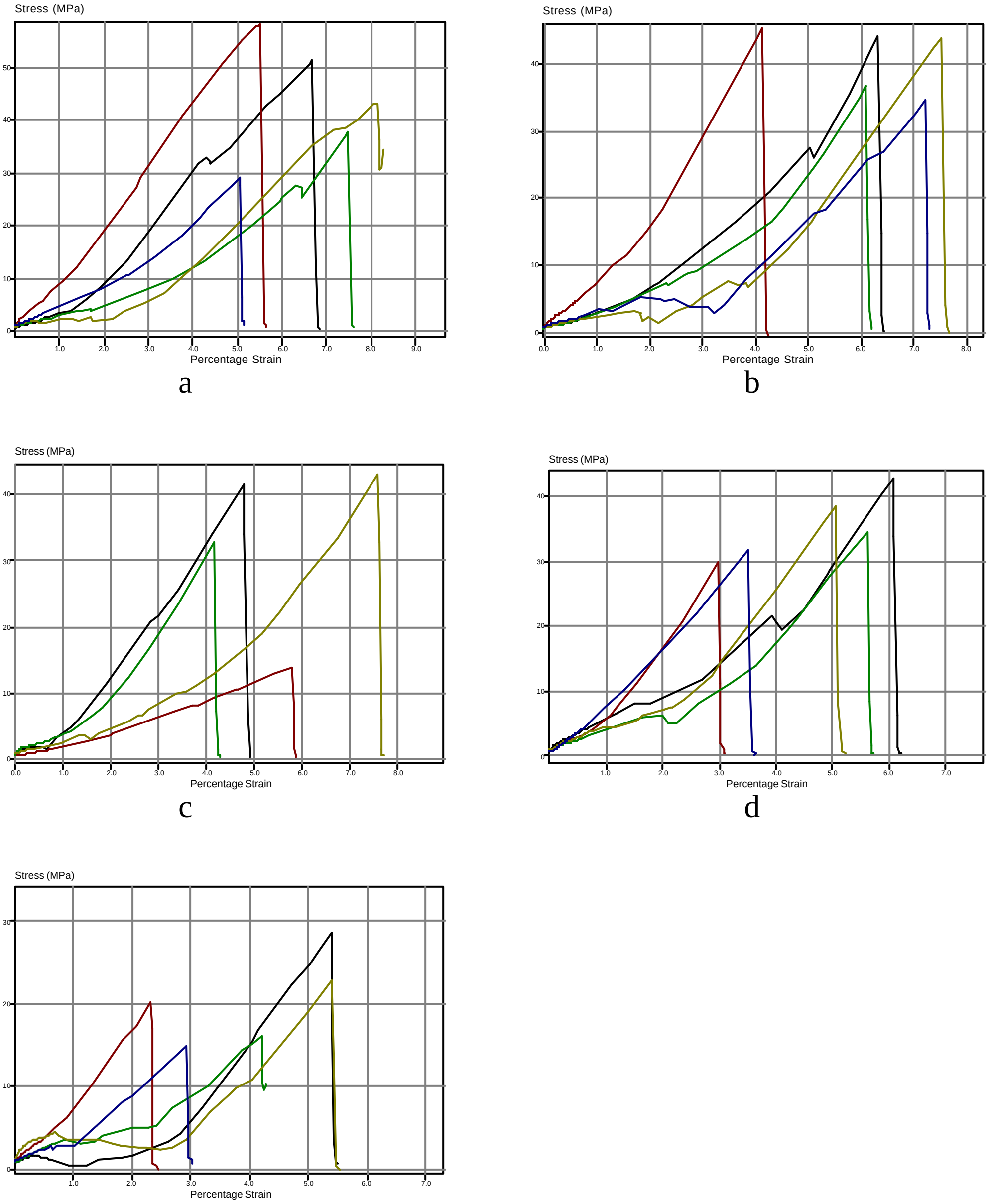


Figure 3.46 DMA Scan of 2 min microwave PMMA- % 5 TLCP mixture

3.9 TENSILE TESTS OF PMMA REINFORCED TLCP

The tensile test curves and results of PMMA, TLCP and PMMA-TLCP mixtures containing % 0.5 – 2 – 5 TLCP are given in Figures 3.47 – 3.51 and the results are tabulated in Tables 3.8-3.12.

For heat cured PMMA samples (Table 3.8), the stiffness and young's modulus values increased, the tensile strength and percent strain at break decreased by the addition of TLCP. From Figure 3.39, it is seen that these blends do not have yield. They have a hard and brittle structure due to their highly crosslinked structure and high molecular weight. The change of the variables are not regular for all of them in the case of increase in percentage of TLCP. However, there is a regularity tendency for stiffness and percent strain. The mechanical variables for 8 days curing period by gamma radiation are very close to that of heat cured sample. However the values are drastically decreased for the shorter period curing. For 30 and 90-min irradiated samples, the tensile curve (Figures 3.40 and 3.41) shows that the samples are ductile and percent strain is higher than highly cured samples (Figures 3.39, 3.42 and 3.43). There is a considerable increase in values of stiffness and young's modulus of PMMA with addition of TLCP but not statistically significant difference for tensile strength and percent strain. However there is no regular trend change with percentage of TLCP in PMMA. The mechanical properties for the microwave curing (Table 3.12) shows the similar trend as that of the heat curing, but the values are much smaller. This is most probably due to the nature of curing. In the first stage of polymerization (60°C for half hour) more rest monomer remain in the polymer matrix. Since in microwave oven high temperature is reached in short time, the monomer evaporates giving bubbles in the material, which weaken the mechanical strength.



a

b

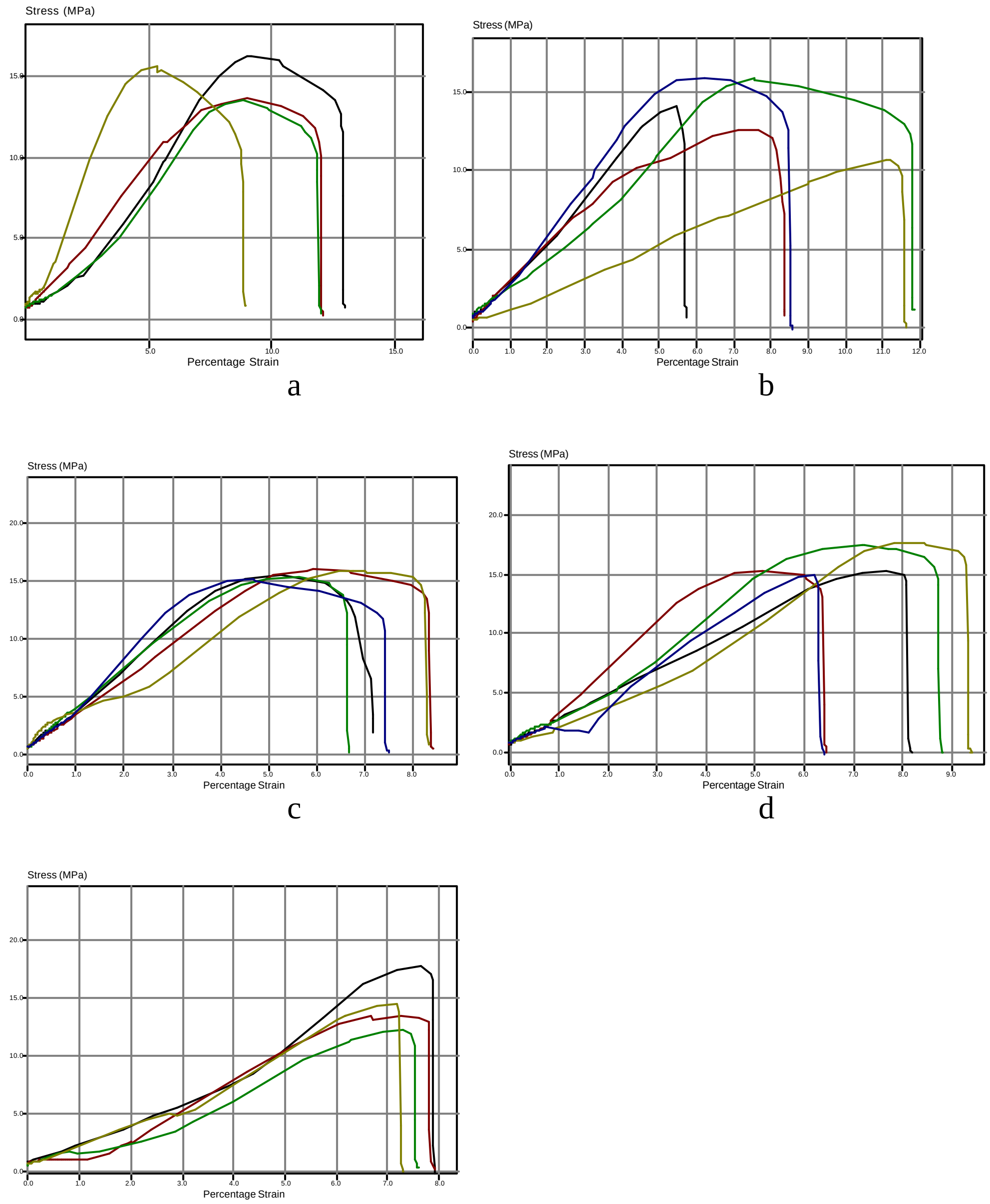
c

d

e

Figure 3.47 The Stress-Strain curves of heat cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture



a

b

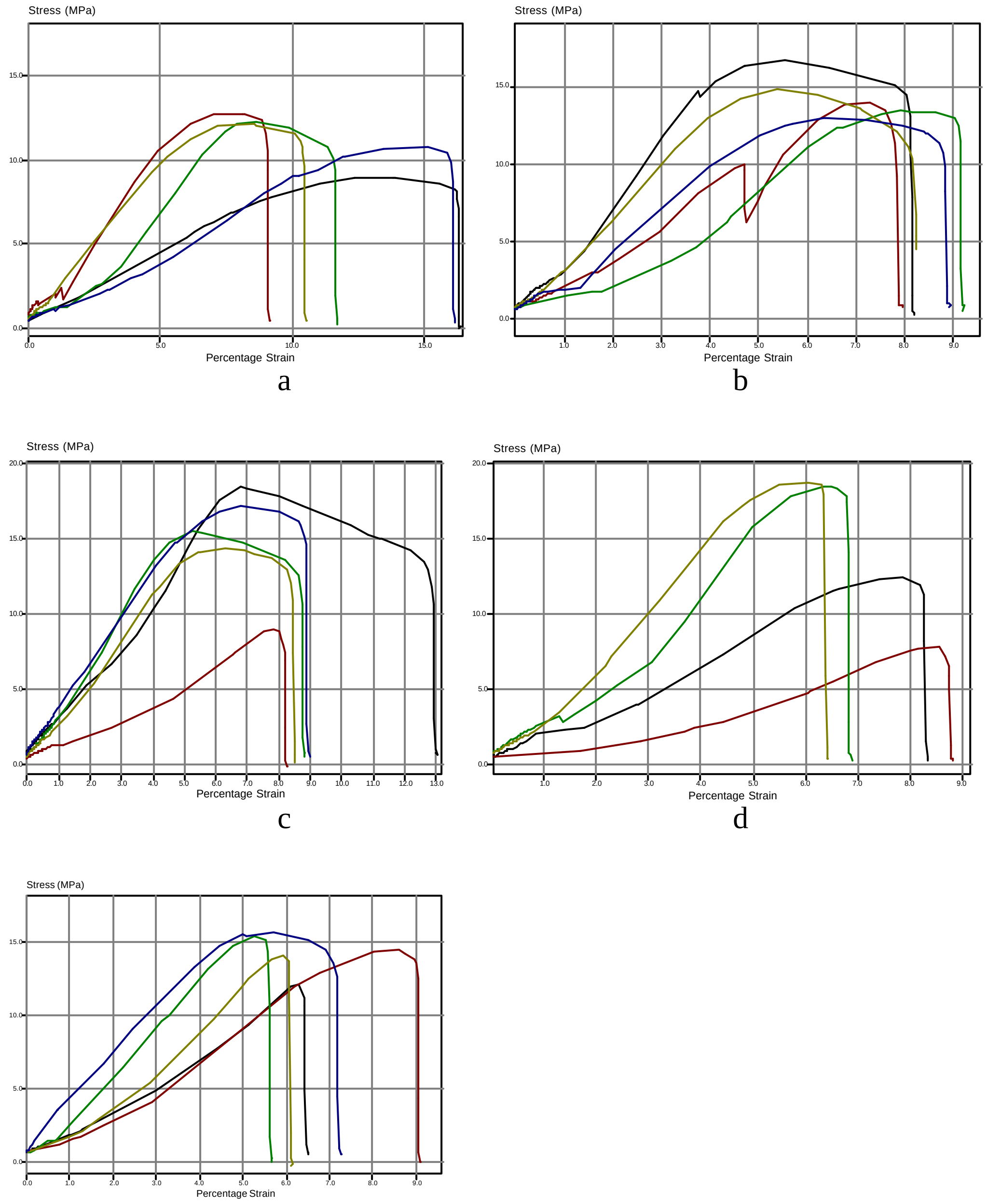
c

d

e

Figure 3.48 The Stress-Strain curves of 30 min gamma cured

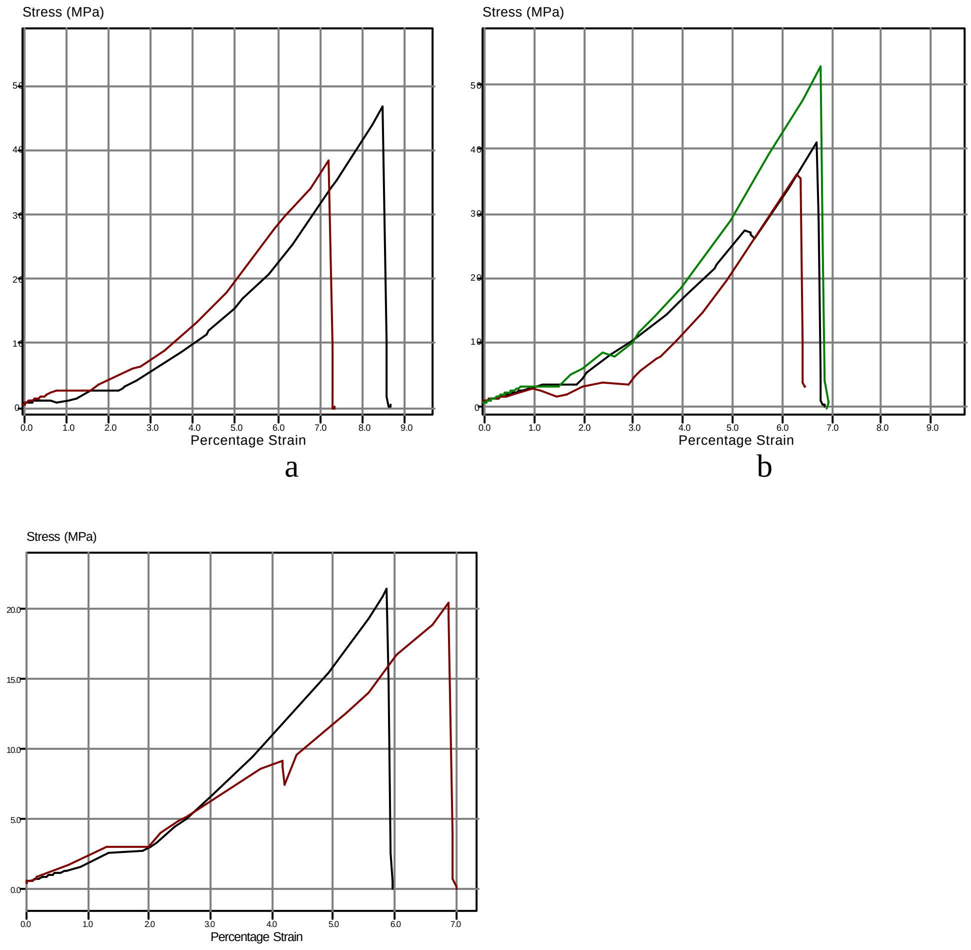
a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture



a b c d e

Figure 3.49 The Stress-Strain curves of 90 min gamma cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture



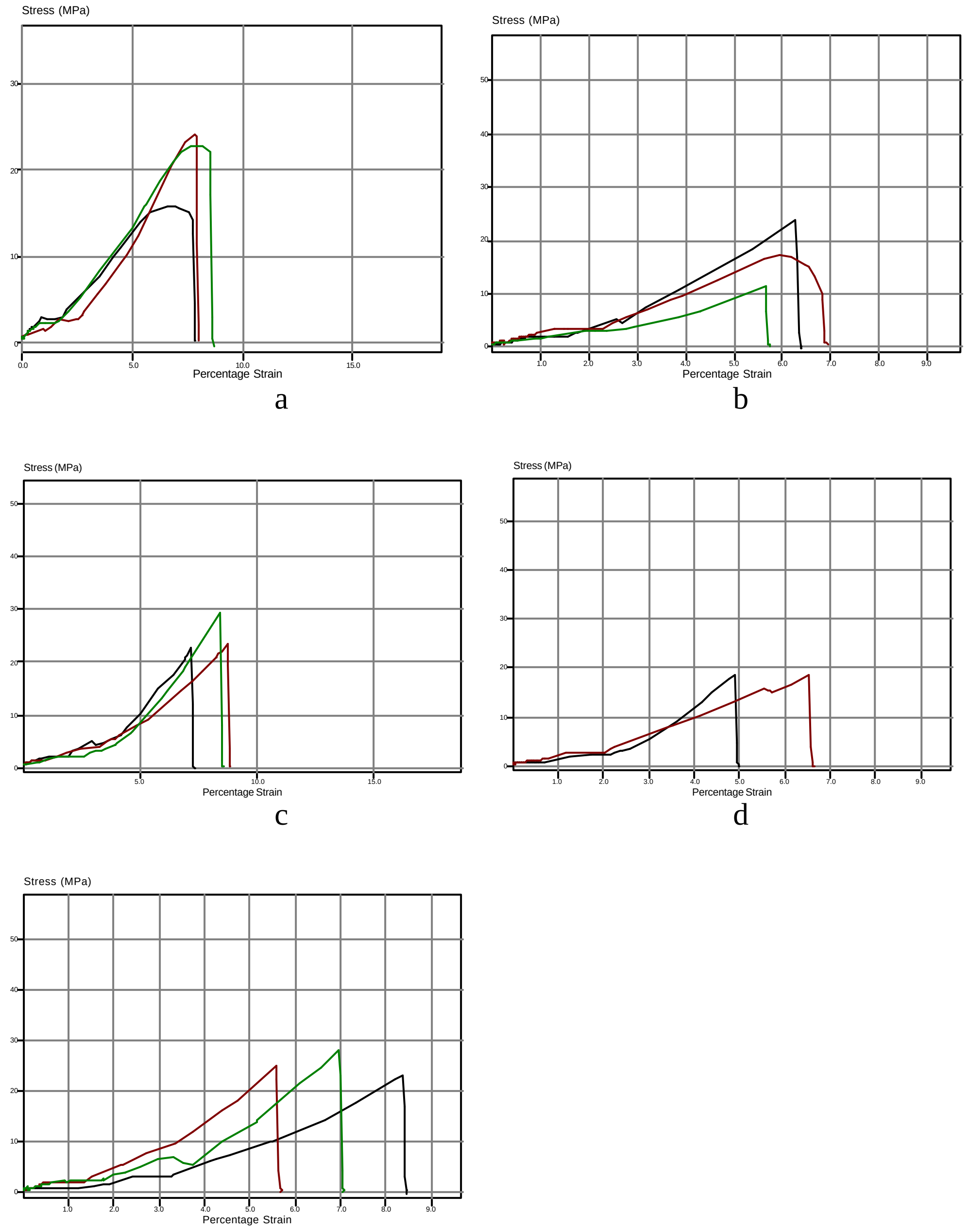
a

b

c

Figure 3.50 The Stress-Strain curves of 8 day gamma cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture



a b

c d

e

Figure 3.51 The Stress-Strain curves of 2 min microwave cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture

Table 3.8 Tensile Test Results of 60 min heat cured PMMA-TLCP mixtures

% TLCP + Heat cured PMMA (60 min)	Stiffness (kN/m)		Tensile Strength (MPa)		Young’s Modulus (GPa)		% Strain at break	
	MV	SD	MV	SD	MV	SD	MV	SD
PMMA	183	50	44	6	0.9	0.05	6.6	1.2
0.5	201	24	40	4	1.1	0.04	6.3	1.2
0.5+silane	206	45	33	5	1.3	0.06	5.6	1.3
2	228	24	36	4	1.2	0.05	4.7	1.2
5	265	50	21	4	1.1	0.06	4.1	1.3

Table 3.9 Tensile Test Results of 30 min gamma cured PMMA-TLCP mixtures

% TLCP + Gamma cured PMMA (30 min)	Stiffness (kN/m)		Tensile Strength (MPa)		Young’s Modulus (MPa)		% Strain at break	
	MV	SD	MV	SD	MV	SD	MV	SD
PMMA	59	10	12	5	445	9	11	1.5
0.5	59	14	14	2	308	11	9	2
0.5+silane	69	15	16	0.4	329	8	10	3
2	69	16	16	1.2	386	12	7.7	1.2
5	54	19	14	2	311	13	7.5	0.3

Table 3.10 Tensile Test Results of 90 min gamma cured PMMA-TLCP mixtures

% TLCP + Gamma cured PMMA (90 min)	Stiffness (kN/m)		Tensile Strength (MPa)		Young’s Modulus (MPa)		% Strain at break	
	MV	SD	MV	SD	MV	SD	MV	SD
PMMA	40	9	11	1.4	312	13	13	3
0.5	66	12	14	1.3	250	14	8.3	0.5
0.5+silane	61	8	15	3	298	11	9.4	1.8
2	63	7	14	4	300	12	7.5	1
5	59	12	14	1.2	275	13	6.8	1.2

Table 3.11 Tensile Test Results of 8 day gamma cured PMMA-TLCP mixtures

% TLCP + Gamma cured PMMA (8 days)	Stiffness (kN/m)		Tensile Strength (MPa)		Young’s Modulus (MPa)		% Strain at break	
	MV	SD	MV	SD	MV	SD	MV	SD
PMMA	213	14	43	4	1015	12	7.9	0.7
0.5	197	15	36	2	1251	17	6.6	0.2
0.5+silane	160	14	20	3	691	13	6.4	0.5

Table 3.12 Tensile Test Results of 2 min microwave cured PMMA-TLCP mixtures

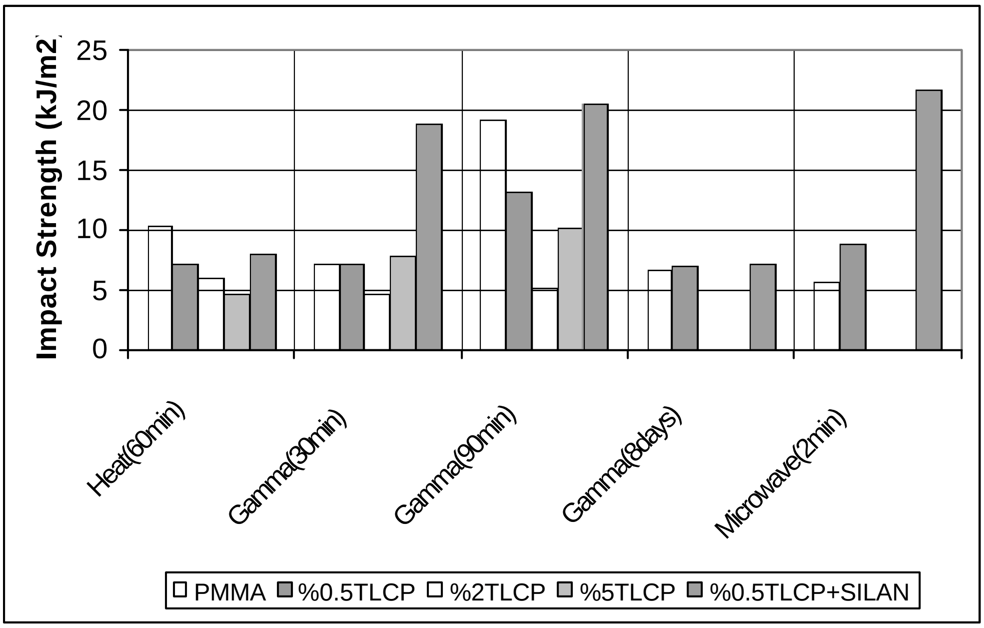
% TLCP + Microwave cured PMMA (2 min)	Stiffness (kN/m)		Tensile Strength (MPa)		Young’s Modulus (MPa)		% Strain at break	
	MV	SD	MV	SD	MV	SD	MV	SD
PMMA	91	19	21	3	437	25	8	0.4
0.5	120	25	18	5	534	22	6	0.4
0.5+silane	147	22	25	3	684	23	8	0.6
2	175	22	17	2	610	25	8.7	2
5	162	26	25	2	670	27	6.9	1

3.10 IMPACT TESTS OF PMMA REINFORCED WITH TLCP

The impact test results of PMMA containing % 0.5 – 2 – 5 and silane treated % 0.5 TLCP are given in Table 3.13.

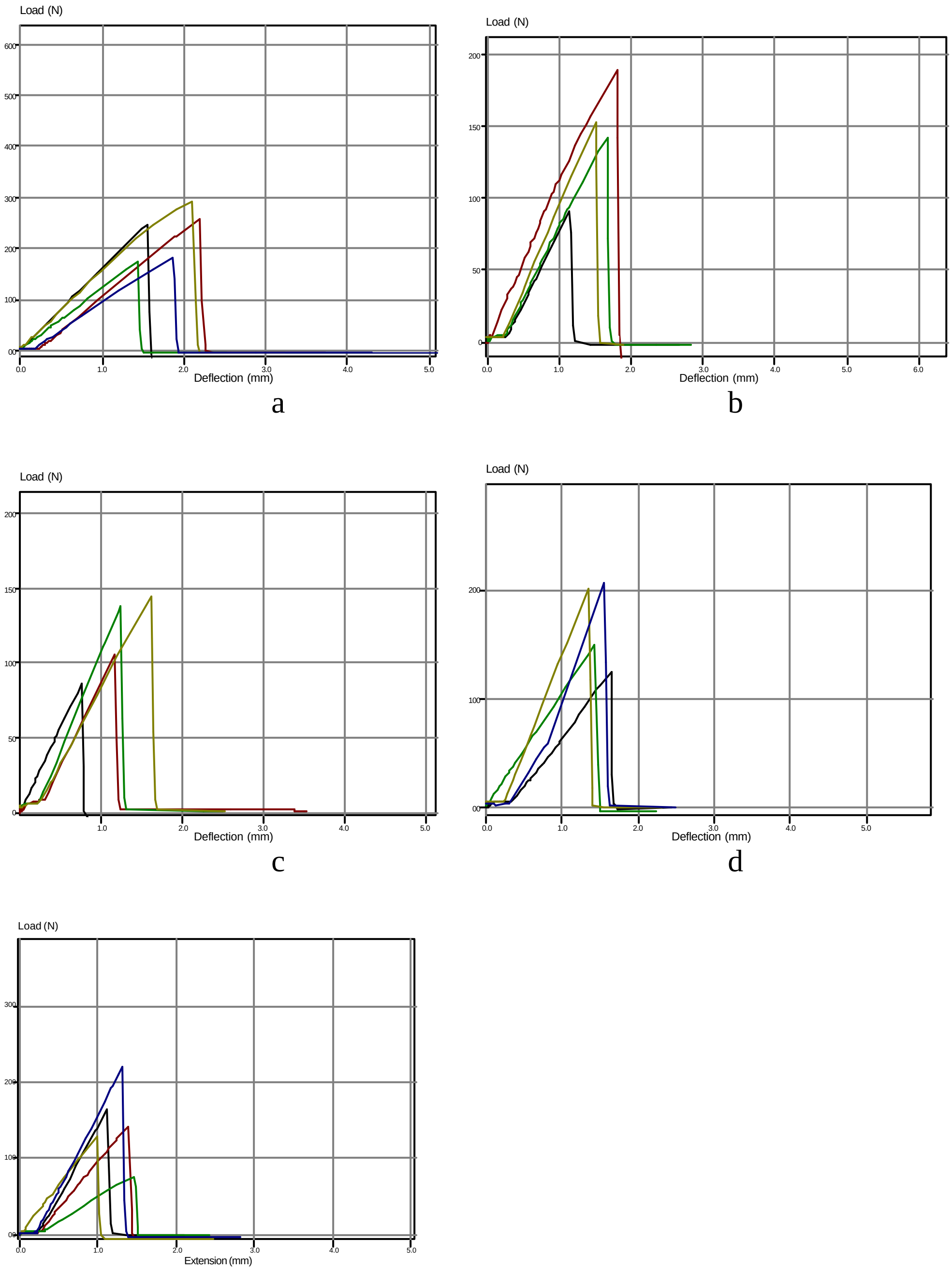
For heat cured PMMA-TLCP mixtures, the impact strength decreased by the addition of TLCP. The increasing TLCP concentration causes formation of more voids in the material which decrease the impact strength. The increase in the silane coupling shows that the interaction of TLCP with PMMA is increased. For 30 gamma cured PMMA-TLCP mixtures, impact strength increased by the addition of TLCP. As 30 min is not enough to have fully crosslinked PMMA, TLCP acted as toughener. Silane effect is so high that a strong physical bonding is achieved between PMMA and TLCP. For 90-min gamma cured PMMA-TLCP mixtures impact strength is lowered by the addition of TLCP. For 8-day gamma curing, the trend is much improved but still it is not increased as expected. This is most probably due to the polymerization of material is just completed and the considerable crosslinking has not been achieved yet. For 2-min microwave curing, the expected increase in impact with silane coupled TLCP is observed. This indicates a better material interaction.

Table 3.13 Impact Results of heat, gamma and microwave cured PMMA



3.11 THREE POINT BENDING TESTS OF PMMA REINFORCED WITH TLCP

The three point test curves and results of PMMA-TLCP mixtures containing % 0.5 – 2 – 5 and silane treated % 0.5 TLCP are given in Figures 3.52-3.56 and Tables 3.14-3.18. For heat cured, 30 min and 90 min gamma cured PMMA-TLCP mixtures, the flexural strength, modulus, strain values decreased by the addition of TLCP. For 8-day gamma cured and 2-min microwave PMMA-TLCP mixtures, flexural strength and strain decreased whereas flexural modulus slightly increased. This increase is not so high to be considerable.



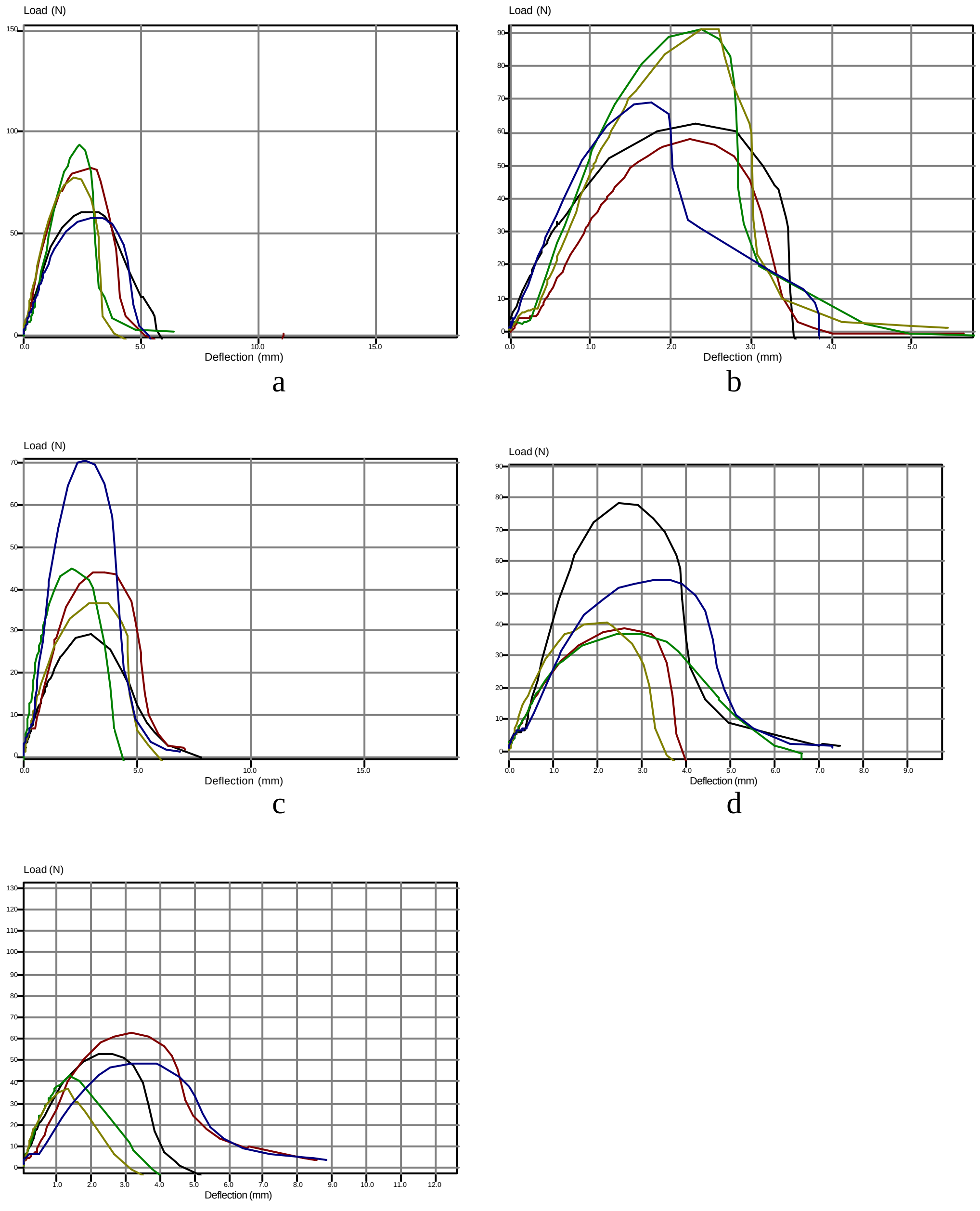
a b

c d

e

Figure 3.52 The Load-Deflection Curves of Three Point Bending Test of heat cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture



a

b

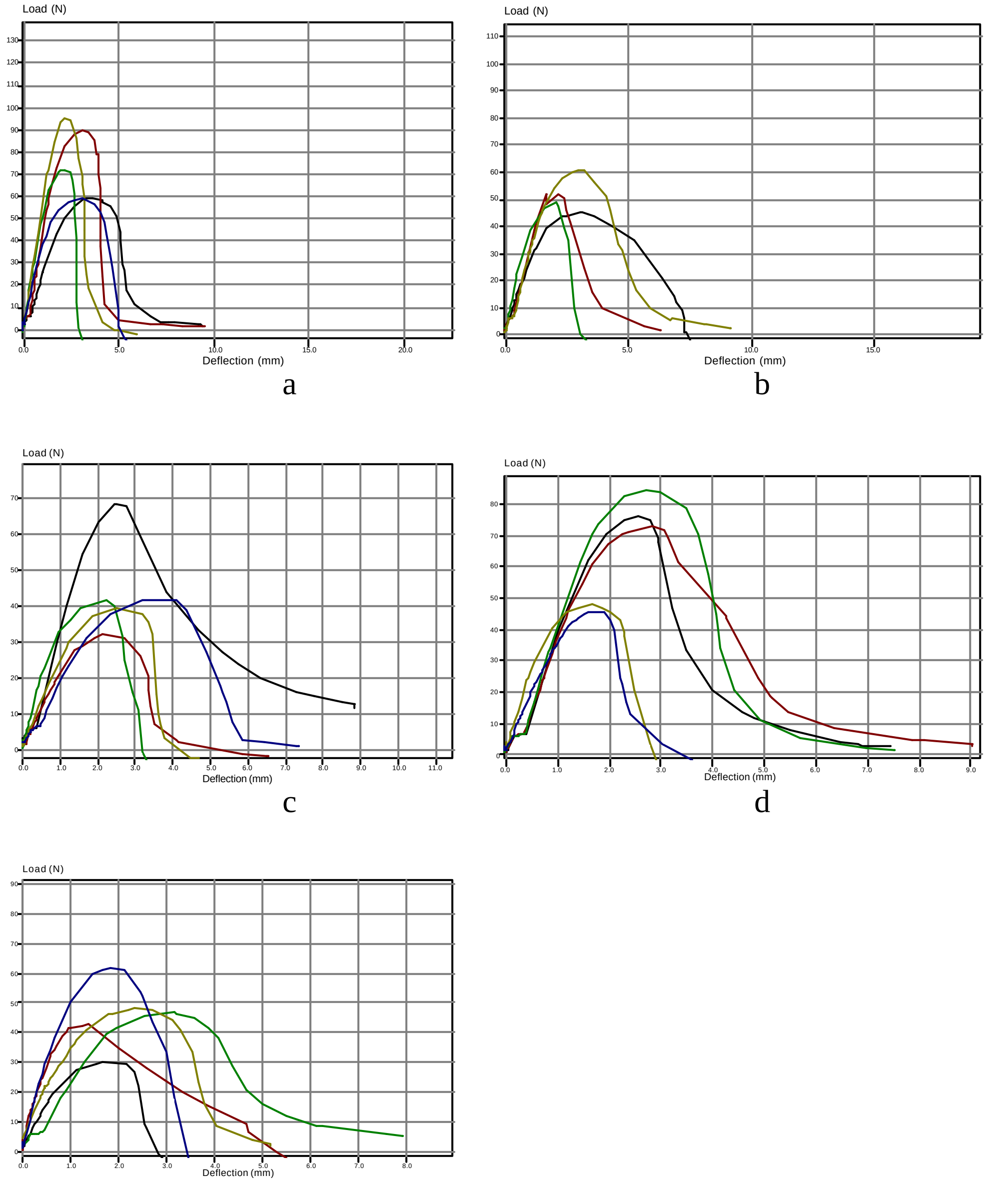
c

d

e

Figure 3.53 The Load-Deflection Curves of Three Point Bending Test of 30 min gamma cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture



a

b

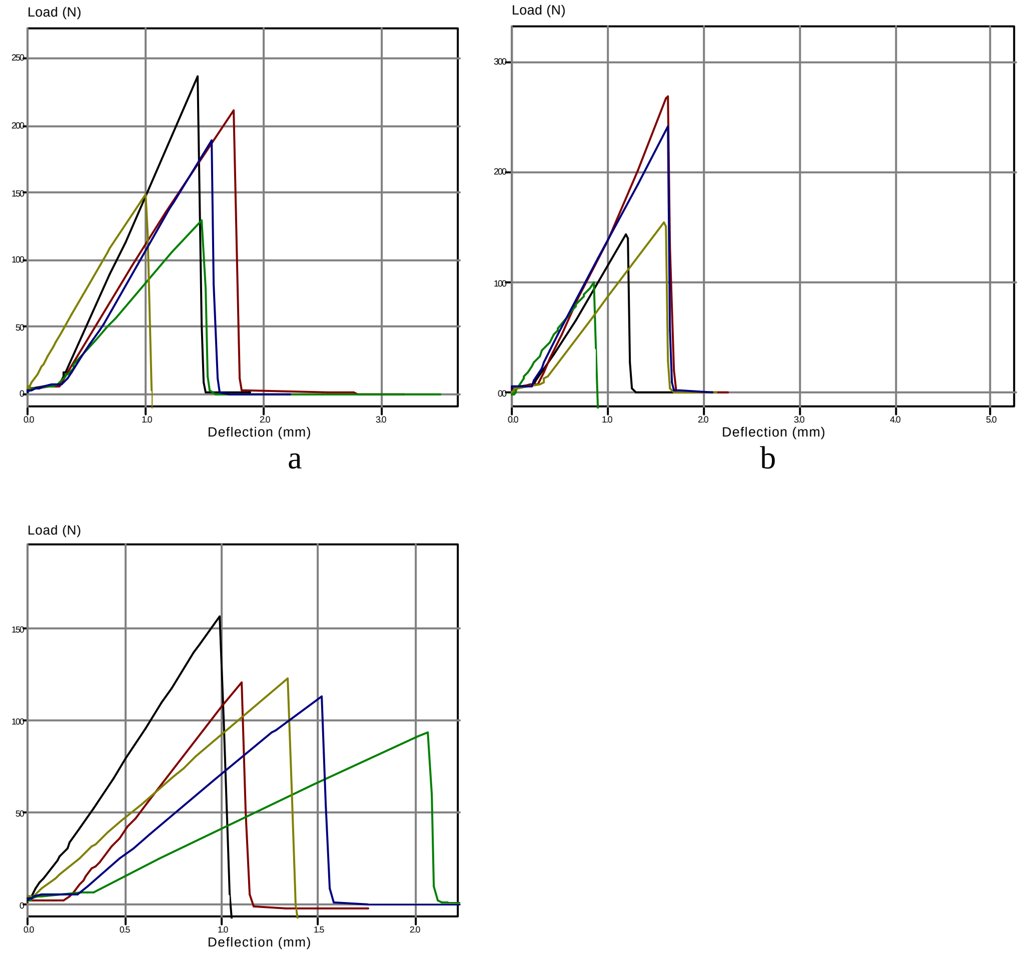
c

d

e

Figure 3.54 The Load-Deflection Curves of Three Point Bending Test of 90 min gamma cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture



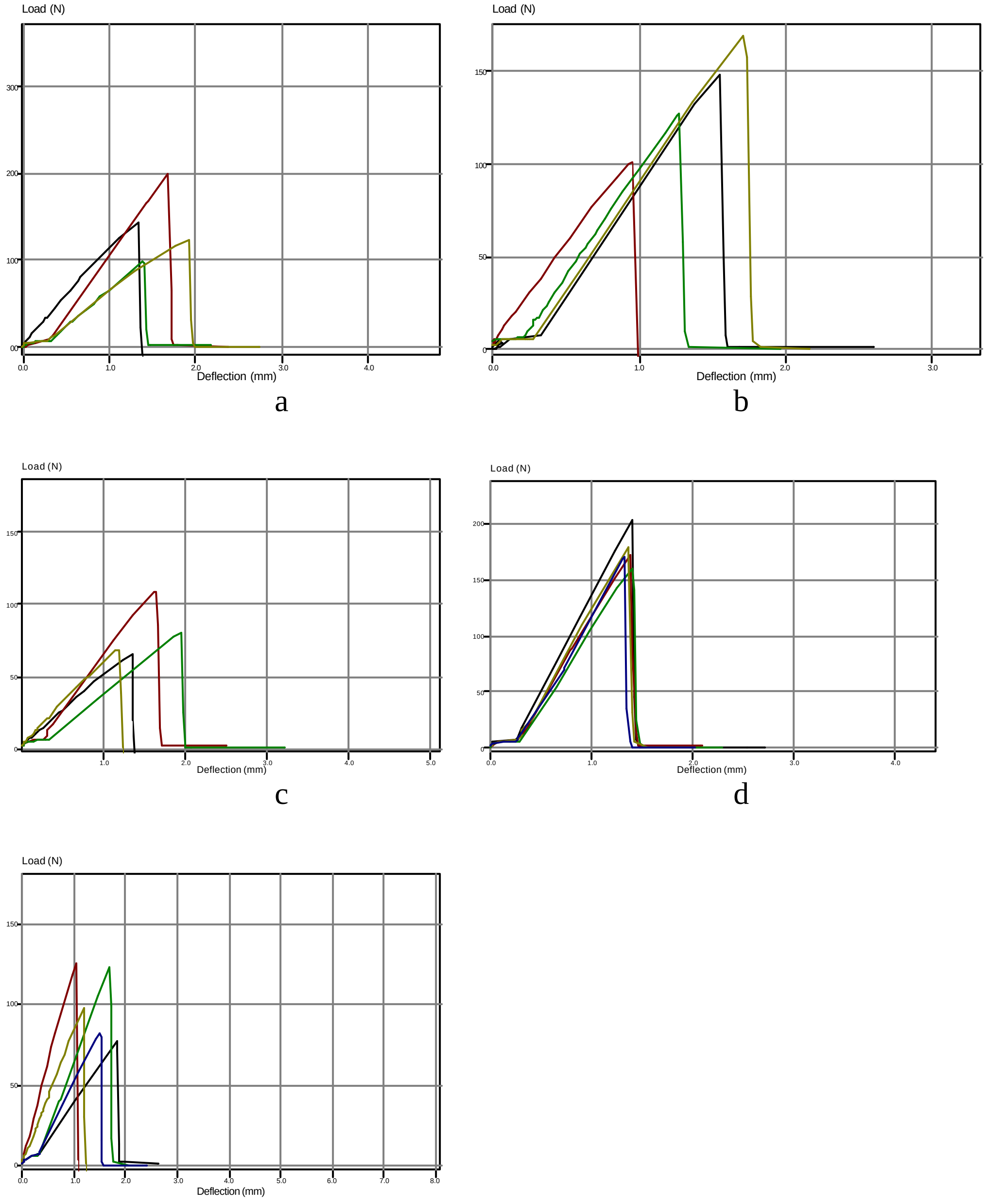
a

b

c

Figure 3.55 The Load-Deflection Curves of Three Point Bending Test of 8 day gamma cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture



a

b

c

d

e

Figure 3.56 The Load-Deflection Curves of Three Point Bending Test of 2 min microwave cured

a) PMMA
b) PMMA-% 0.5 TLCP mixture
c) PMMA-silane treated % 0.5 TLCP mixture
d) PMMA-% 2 TLCP mixture
e) PMMA-% 5 TLCP mixture

Table 3.14 The Results of Three point Bending Tests of Heat Cured Samples

Heat cured	Flexural Strength MPa (s_{fs})		Flexural Modulus MPa (E_B)		Flexural Strain (r)	
	MV	SD	MV	SD	MV	SD
PMMA	75.4	8.2	2246	300	0.03	0.01
PMMA+% 0.5 TLCP	59.1	10	1964	315	0.02	0
PMMA+silane treated % 0.5 TLCP	35.3	9	1686	260	0.02	0.01
PMMA+% 2 TLCP	56.8	2	2673	142	0.03	0
PMMA+% 5 TLCP	36	10	1570	273	0.03	0.01

Table 3.15 The Results of Three point Bending Tests of 30 min Gamma Cured Samples

30 min gamma cured	Flexural Strength MPa (s_{fs})		Flexural Modulus MPa (E_B)		Flexural Strain (r)	
	MV	SD	MV	SD	MV	SD
PMMA	27	3.8	736	50	0.05	0.01
PMMA+% 0.5 TLCP	24	6	630	45	0.04	0.01
PMMA+silane treated % 0.5 TLCP	18	2.7	492	69	0.05	0.01
PMMA+% 2 TLCP	21.5	4.8	638	97	0.04	0.01
PMMA+% 5 TLCP	19	4	583	87	0.04	0.02

Table 3.16 The Results of Three point Bending Tests of 90 min Gamma Cured Samples

90 min gamma cured	Flexural Strength MPa (s_{fs})		Flexural Modulus MPa (E_B)		Flexural Strain (r)	
	MV	SD	MV	SD	MV	SD
PMMA	26.6	2	705	46	0.05	0.01
PMMA+ % 0.5 TLCP	21.4	3	617	50	0.05	0.01
PMMA+ silane treated % 0.5 TLCP	19	4	560	54	0.04	0.01
PMMA+% 2 TLCP	21	5	626	21	0.04	0.01
PMMA+% 5 TLCP	16.5	3	530	51	0.04	0.01

Table 3.17 The Results of Three point Bending Tests of 8 day Gamma Cured Samples

8 day gamma cured	Flexural Strength MPa (s_{fs})		Flexural Modulus MPa (E_B)		Flexural Strain (r)	
	MV	SD	MV	SD	MV	SD
PMMA	58	10	2354	268	0.03	0.01
PMMA+% 0.5 TLCP	48	4	2312	240	0.03	0.01
PMMA+silane treated % 0.5 TLCP	53	4	2688	204	0.02	0

Table 3.18 The Results of Three point Bending Tests of 2 min Microwave Cured Samples

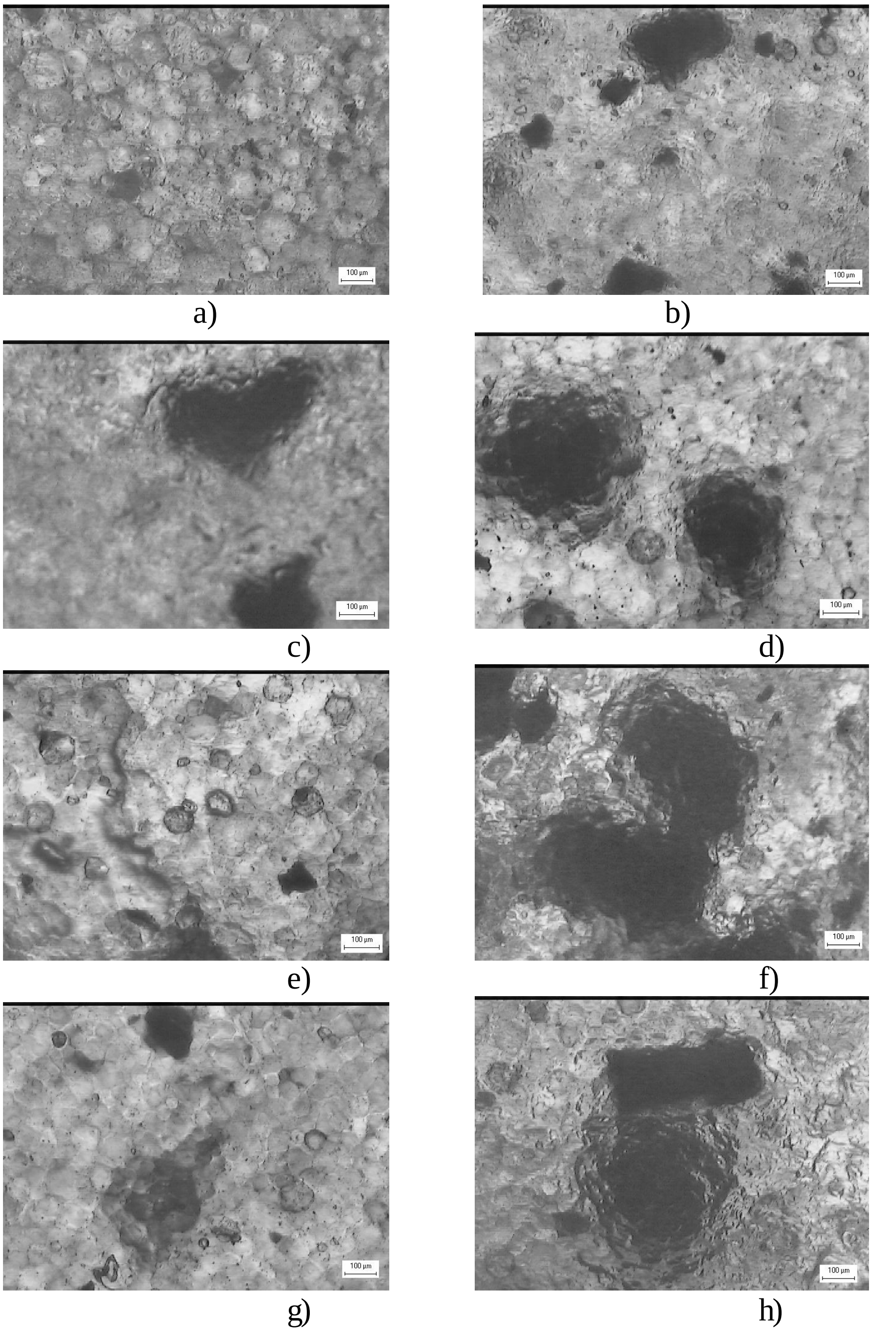
2 min microwave cured	Flexural Strength MPa (s_{fs})		Flexural Modulus MPa (E_B)		Flexural Strain (r)	
	MV	SD	MV	SD	MV	SD
PMMA	44	9	1712	280	0.03	0
PMMA+% 0.5 TLCP	40	7	1642	228	0.03	0
PMMA+silane treated % 0.5 TLCP	34	4	1499	255	0.03	0.01
PMMA+% 2 TLCP	46	5	1974	229	0.03	0
PMMA+% 5 TLCP	42	7	1943	271	0.02	0

3.12 LIGHT MICROSCOPE IMAGES OF PMMA REINFORCED WITH TLCP

From the optical images (Figure 3.57), the following general results were observed:

1. In most of the samples, the spherical powder polymer retains their original forms. Therefore, polymerization of the monomer (liquid) takes place without addition to the powder polymer. This gives a heteregeneous property of the final sample.
2. The distribution of TLCP in PMMA is not homogeneous and in most images two phases were observed (TLCP and PMMA phases).
3. In heat curing samples, the powder particle size from the surface are predominant, while in microwave curing there is a film layer on the surface for most of the samples. This is because microwave produces high temperature in the inner part of the sample where heat curing starts from surface slowly proceeding in the sample. As a result, the rest monomer in the matrix of the sample evaporates as well as polymerizing in microwave curing, however in heat curing the evaporation rate is much smaller than polymerization rate.

4. In gamma curing, the radiation penetrates into sample matrix homogeneously without increasing the temperature to the evaporation temperature of the monomer. The polymerization will be completed if enough doses of radiation is given. Therefore for the 8-day curing the polymerization and curing is almost completed while for 30-min and 90-min gamma curing periods, the polymerization and/or crosslinking is not completed.



a) b) c) d) e) f) g) h)

Figure 3.57 Light microscope images of

a) and b) 60 min heat cured PMMA-% 0.5 TLCP mixture, c) 30-min gamma cured PMMA-% 0.5 TLCP mixture, d) and e) 90-min gamma cured PMMA-% 0.5 TLCP mixture, f) 90 min cured gamma cured PMMA-% 5 TLCP mixture, g) 8-day gamma cured PMMA-% 0.5 TLCP mixture, h) 2-min microwave cured PMMA-silane treated % 0.5 TLCP mixture.

CHAPTER 4

CONCLUSION

From the results of this experimental investigation the following conclusions can be mentioned:

1. In FT-IR spectrum of TLCP, ester exchange reactions' peak was observed for PET and PABA.

2. In DSC thermogram of TLCP, two T_g values were observed so that a block copolymer containing two segments is present.

3. The stiffness and tensile properties of PET decreased by the addition of TLCP. PET has a ductile structure however PET-TLCP blends have hard and brittle structure.

4. In FT-IR and NMR spectra of PMMA and PMMA-TLCP mixtures, no peaks were observed that would lead to the presence of chemical bonding between PMMA-TLCP.

5. In DSC thermograms of some PMMA samples, T_c peaks were observed (Table 3.4) shows that curing (crosslinking) has not finished.

6. In DMA spectra of 30-min and 90-min gamma cured PMMA and PMMA-TLCP samples, T_g values were seen at about 68ºC. This shows that the average molecular weight of the samples are low due to incomplete polymerization and crosslinking.

7. Tensile tests's results show that high molecular weight samples have hard and brittle structure whereas low molecular weight samples have ductile structure. Percentage strain is higher for ductile structured samples whereas tensile strength, modulus, stiffness are higher for brittle structured samples.

8. Impact tests's results show that high impact values were observed for silane treated samples. This is because silane form a physical bonding between PMMA and TLCP.

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