CHAPTER 3

EXPERIMENTAL METHODS AND RESULTS

3.1 Chemicals, Apparatus and Instruments

3.1.1 Chemicals

The various chemicals used in this research were as shown in Table 3.1.

Table 3.1 : Chemicals used in this research.

Chemical	Usage	Grade	Supplier
2-Hydroxyethyl methacrylate	monomer	95%	Fluka
Butyl acrylate	monomer	lab. reagent	BDH Chemicals
Methyl acrylate	monomer	99.5%	Fluka
Ethylene glycol dimethacrylate	crosslinking agent	> 97%	Fluka
Benzoyl peroxide	free radical initiator	lab. reagent	BDH Chemicals
Copper(I) chloride	stabilizer	lab. reagent	Merck
Molecular sieves Type 4Å	drying agent	lab. reagent	Fluka
Silica gel	drying agent	lab. reagent	BDH Chemicals
Acetone	solvent	lab. reagent	Lab-Scan
Benzene	solvent	lab. reagent	Merck
Chloroform	solvent	lab. reagent	Merck
Dimethyl sulfoxide	solvent	lab. reagent	Fluka
Ethanol	solvent	lab. reagent	Merck
Methanol	solvent	com. grade	BDH Chemicals

Table 3.1 (continued)

Chemical	Usage	Grade	Supplier
Toluene	solvent	lab. reagent	Merck
Water	immersion medium	deionized	-
Poly(ethylene terephthalate) film	mould release agent	commercial	3M
Polytetrafluoroethylene tape	gasket	commercial	-

3.1.2. Apparatus and Instruments

The major items of equipment used in this research were as shown in Table 3.2.

Table 3.2 : Apparatus and instruments used in this research.

Apparatus and Instruments	Company	Model
Drying oven	Whatman	FCO - 100
Vacuum oven	Eyela	VOS - 300SD
Incubator	Memmert	-
FT-IR Spectrometer	Nicolet	510
Elemental Analyzer (CHNS/O)	Perkin - Elmer	PE - 2400 Series II
Differential Scanning Calorimeter	Perkin - Elmer	DSC 7
Thermogravimetric Analyzer	Perkin - Elmer	TGA 7
KBr press	Jasco	-
Tensile Specimen Press	Kao Tieh	KT - 7016
Mechanical Tester	Instron Corporation	Series 5500

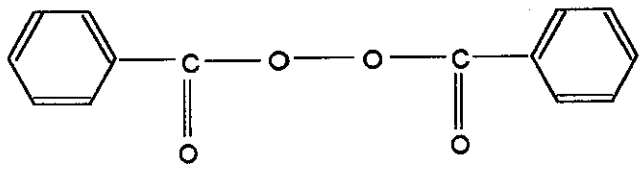
3.2 Purifications and Analyses of Initiator, Crosslinking Agent and Monomers

3.2.1 Recrystallisation of Initiator

Benzoyl peroxide is widely used in polymer chemistry as a source of free radicals for initiation in free-radical polymerisation. The benzoyl peroxide used in this research needed to be purified by recrystallisation before it could be used in polymerisation. This recrystallisation was carried out by first dissolving about 10.0 g of the crude benzoyl peroxide in 25.0 ml of chloroform. After the aqueous layer had been separated off and discarded, the chloroform layer was warmed gently to about 40.0°C. Then, about 75.0 ml of methanol were added and the mixture allowed to cool. The recrystallised benzoyl peroxide was filtered off in a Buchner funnel under a gentle vacuum and washed with more methanol. Finally, the crystals were dried on a clean filter paper at room temperature before being stored in a vacuum desiccator until required for use.

The FT-IR spectrum of the recrystallised benzoyl peroxide is shown in Figure 3.1 and can be compared with a reference spectrum in Figure 3.2. The infrared absorption band assignments are given in Table 3.3.

The benzoyl peroxide sample for IR analysis was prepared in the form of a KBr disc. The chemical structure of benzoyl peroxide is as shown below :



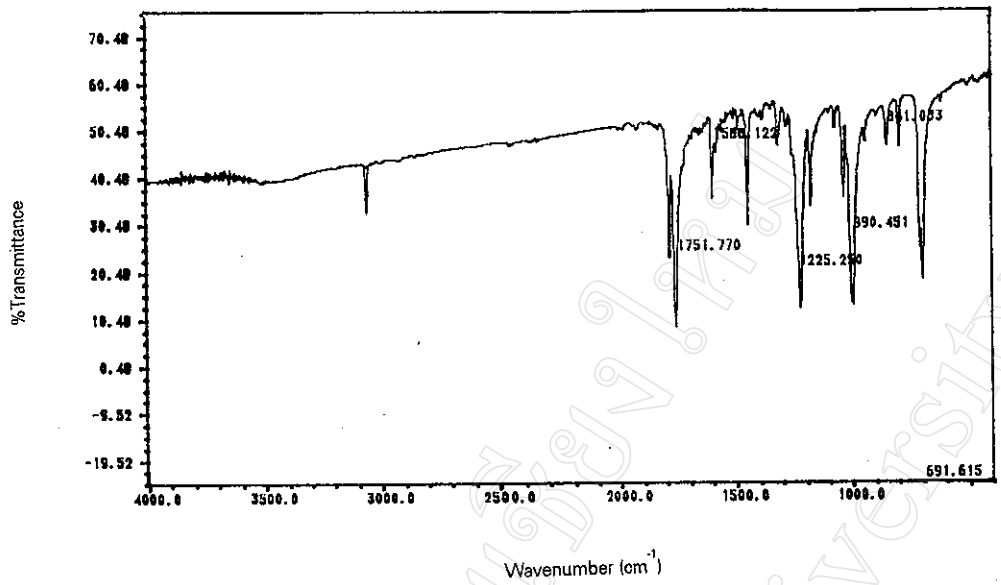


Figure 3.1 : Infrared spectrum of recrystallized benzoyl peroxide.

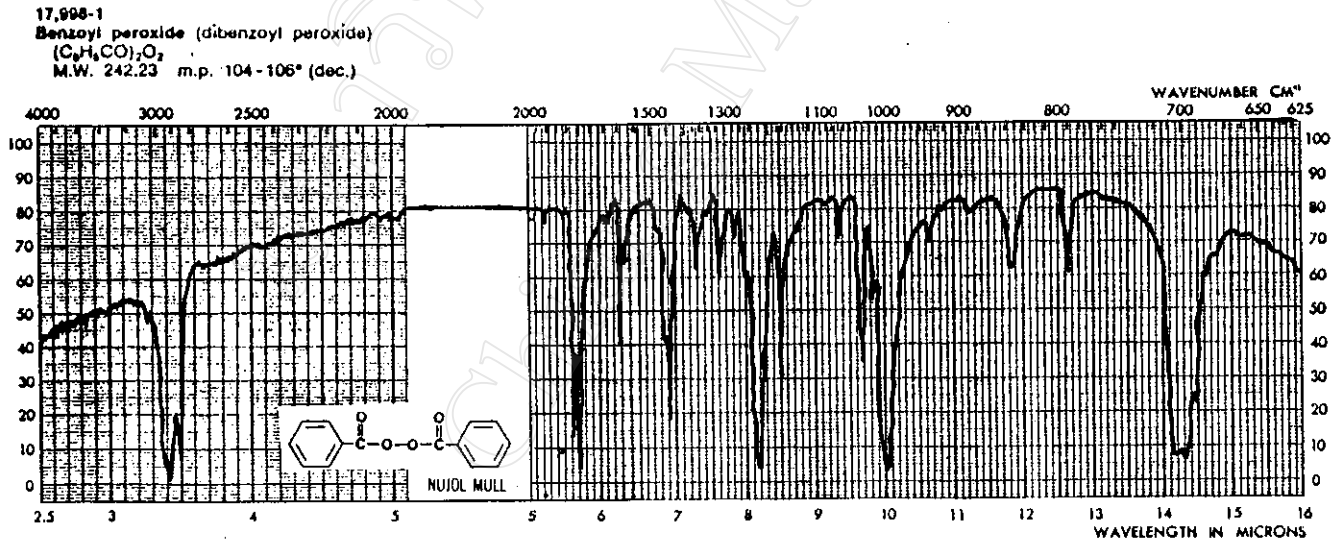


Figure 3.2 : Reference infrared spectrum of benzoyl peroxide [38].

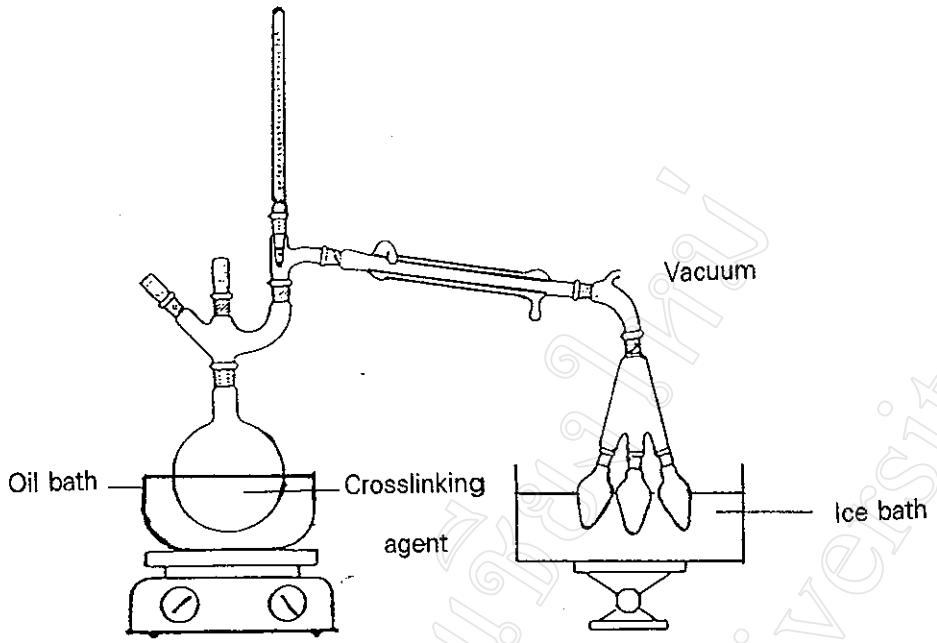
Table 3.3 : Infrared absorption band assignments for recrystallised benzoyl peroxide.

Vibrational Assignments	Wavenumber (cm^{-1})
C=O stretching	1751
O-O stretching	990
C-C stretching, aromatic ring	1588
C-O stretching	1225
C-H stretching, aromatic ring	3100
C-H bending, out-of-plane, aromatic ring	690

3.2.2 Vacuum Distillation of Crosslinking Agent

In this research, the ethylene glycol dimethacrylate used as the crosslinking agent was purified by vacuum distillation. The vacuum distillation apparatus is shown in Figure 3.3. A multi-limb receiver adapter was used which allowed more than one fraction to be collected without disturbing the system. The ethylene glycol dimethacrylate was first dried with molecular sieves 4Å to absorb moisture overnight before vacuum distillation. After decanting the ethylene glycol dimethacrylate away from the drying agent, about 1 g/l of copper(I) chloride was added as stabilizer during distillation. Pure ethylene glycol dimethacrylate was collected as the constant boiling fraction at 99.0°C/ 6 mm Hg pressure (cf. lit. [39] 98-100°C/ 5 mm Hg) and was then stored in the refrigerator until required for use in polymerisation.

The IR spectrum of the distilled crosslinking agent is shown in Figure 3.4 and can be compared with the reference spectrum in Figure 3.5.



Figrure 3.3 : Vacuum distillation apparatus used in the purification of the ethylene glycol dimethacrylate crosslinking agent.

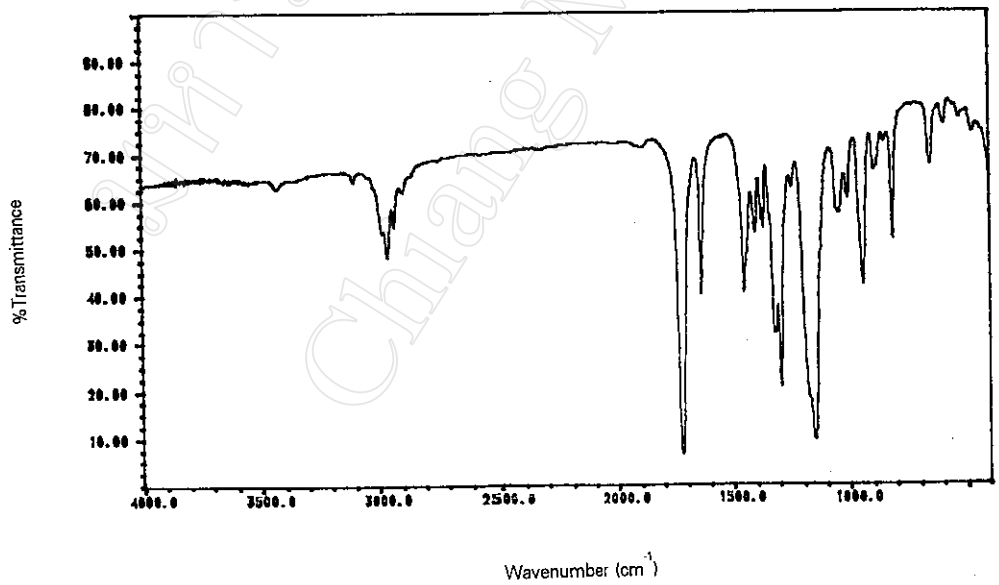


Figure 3.4 : Infrared spectrum of distilled ethylene glycol dimethacrylate.

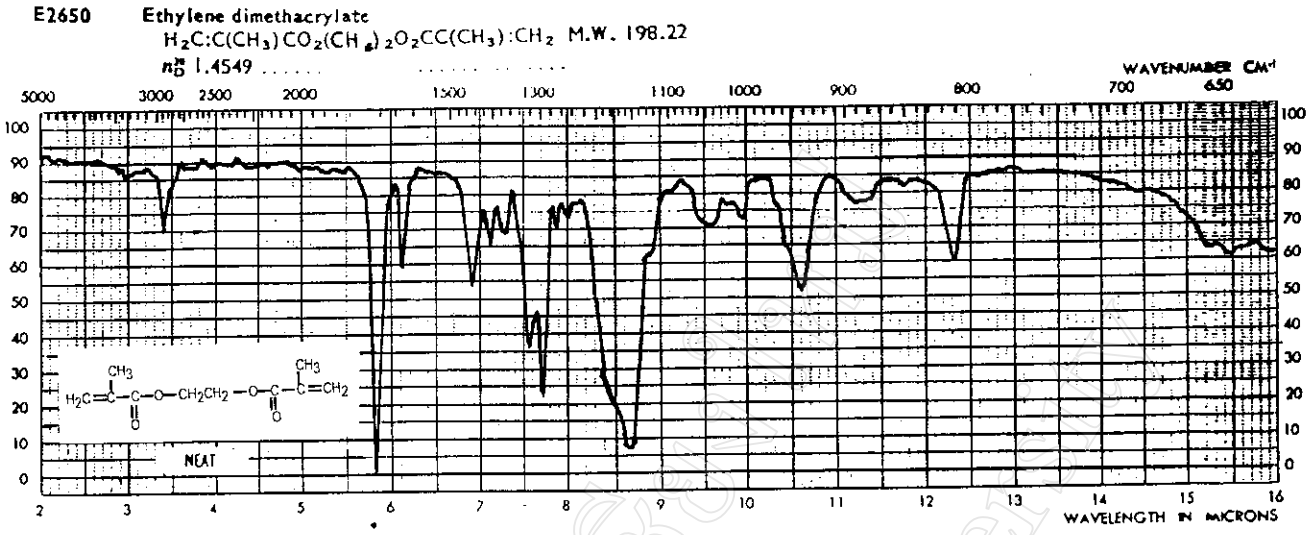


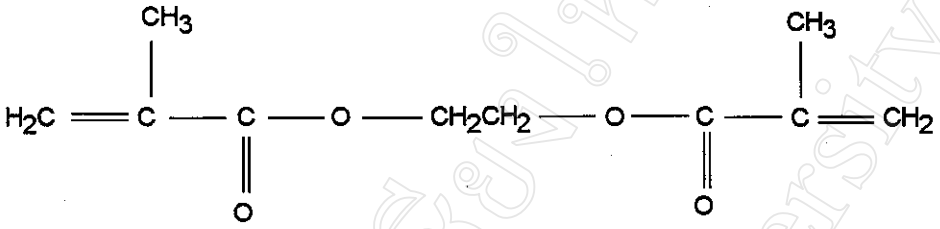
Figure 3.5 : Reference infrared spectrum of ethylene glycol dimethacrylate [38].

The infrared spectrum of the crosslinking agent was obtained from a neat sample contained in a NaCl cell. The major vibrational peaks are listed in Table 3.4.

Table 3.4 : Infrared absorption band assignments for the distilled ethylene glycol dimethacrylate crosslinking agent.

Vibrational Assignments	Wavenumber (cm^{-1})
C-H stretching	2970
C=O stretching	1730
C=C stretching	1650
C-H bending	1470,1420
C-O stretching, acyl-oxygen in C(=O)-O	1300
C-O stretching, alkyl-oxygen in CH_2-O	1150

The chemical structure of ethylene glycol dimethacrylate is as shown below :



3.2.3 Distillation of Monomers

3.2.3.1 2-Hydroxyethyl Methacrylate

The 2-hydroxyethyl methacrylate monomer (Fluka, assay ≈95%) was also purified by vacuum distillation using the same apparatus as for the crosslinking agent (Figure 3.3). Firstly, the 2-hydroxyethyl methacrylate monomer was pre-dried with molecular sieves 4Å to absorb moisture overnight. In the vacuum distillation that followed, pure 2-hydroxyethyl methacrylate was collected as the constant boiling fraction at 75.0°C/ 5 mm Hg pressure(cf. lit. [39] 67°C / 3.5 mm Hg). It was then stored in the refrigerator until required for use in polymerisation.

The IR spectrum of the distilled 2-hydroxyethyl methacrylate is shown in Figure 3.6 and can be compared with the reference spectrum in Figure 3.7.

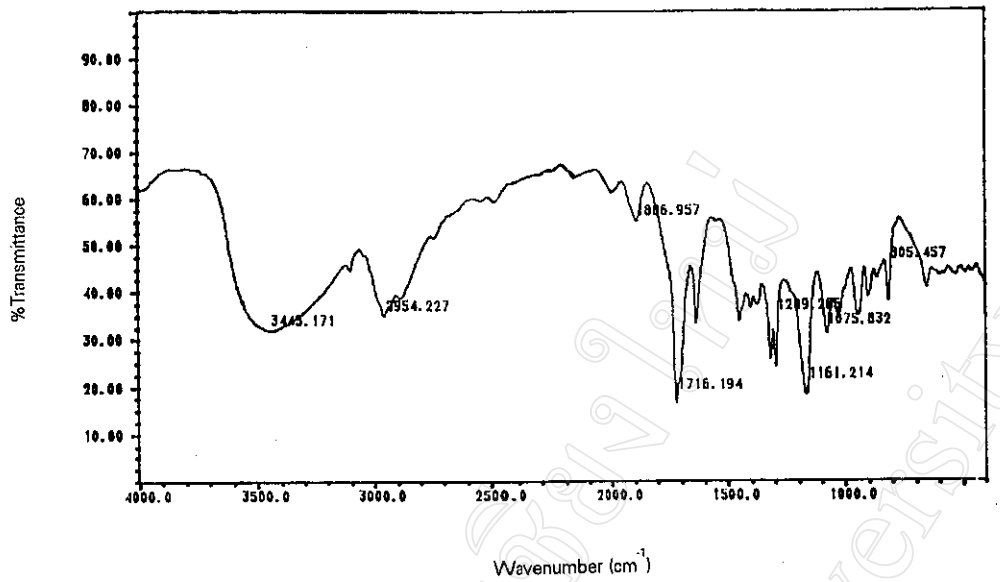


Figure 3.6 : Infrared spectrum of distilled 2-hydroxyethyl methacrylate.

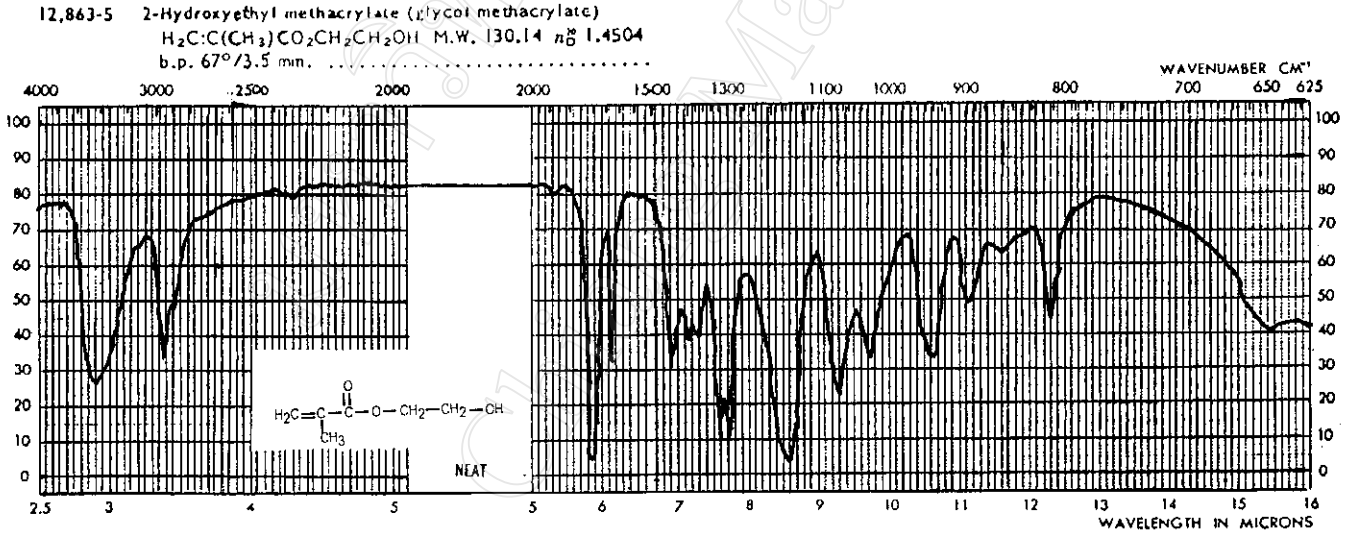


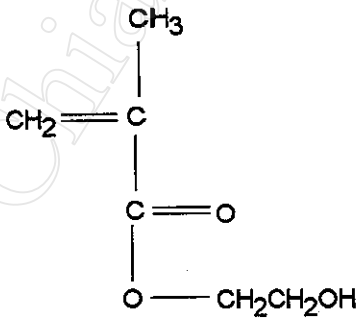
Figure 3.7 : Reference infrared spectrum of 2-hydroxyethyl methacrylate [38].

The major vibrational peaks in Figure 3.6 are assigned as shown in Table 3.5.

Table 3.5 : Infrared absorption band assignments for distilled 2-hydroxyethyl methacrylate monomer.

Vibrational Assignments	Wavenumber (cm^{-1})
O-H stretching	3600 - 3400
C-H stretching	2954
C=O stretching	1716
C=C stretching	1650
C-H bending , in CH_2	1470 , 1420
C-H bending , in CH_3	1320
C-O stretching, acyl-oxygen in C(=O)-O	1290
C-O stretching, alkyl-oxygen in CH_2-O	1161

The chemical structure of 2-hydroxyethyl methacrylate is as shown below :



3.2.3.2 Butyl Acrylate

The butyl acrylate monomer was also purified by vacuum distillation using a similar procedure and apparatus to that for 2-hydroxyethyl methacrylate. The constant boiling fraction at 30.0°C / 6 mm Hg pressure (cf. lit. [39] 145-146°C / 760 mm Hg) was collected and stored in the refrigerator until required for use.

The IR spectrum of the distilled butyl acrylate monomer is shown in Figure 3.8 and the major vibrational peaks assigned in Table 3.6.

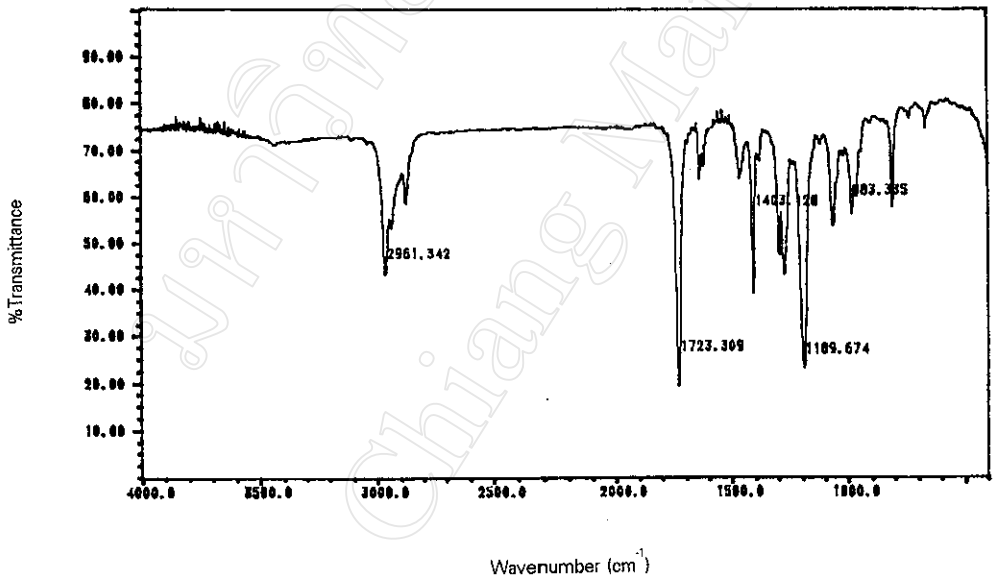
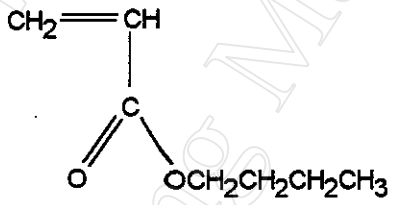


Figure 3.8 : Infrared spectrum of distilled butyl acrylate.

Table 3.6 : Infrared absorption band assignments for the distilled butyl acrylate monomer.

Vibrational Assignments	Wavenumber (cm^{-1})
C-H stretching	2961
C=O stretching	1723
C=C stretching	1650
C-H bending , in CH_2	1480, 1420
C-H bending , in CH_3	1320
C-O stretching, acyl-oxygen in C(=O)-O	1300
C-O stretching, alkyl-oxygen in CH_2-O	1189

The chemical structure of butyl acrylate is as shown below :



3.2.3.3 Methyl Acrylate

The methyl acrylate monomer (Fluka, assay ≈99.5%) was purified by simple distillation under normal atmospheric pressure using the apparatus shown in Figure 3.9.

The methyl acrylate monomer was first dried with molecular sieves 4Å to absorb moisture overnight before distillation. After decanting the methyl acrylate monomer

away from the drying agent, about 1 g/l of copper(I) chloride was added to the monomer as stabilizer. In the distillation that followed, pure methyl acrylate was collected as the constant boiling fraction at 78.0°C/ 730 mm Hg (cf. lit. [39] 78-81°C/ 760 mm Hg) and was stored in a refrigerator until required for use in polymerisation.

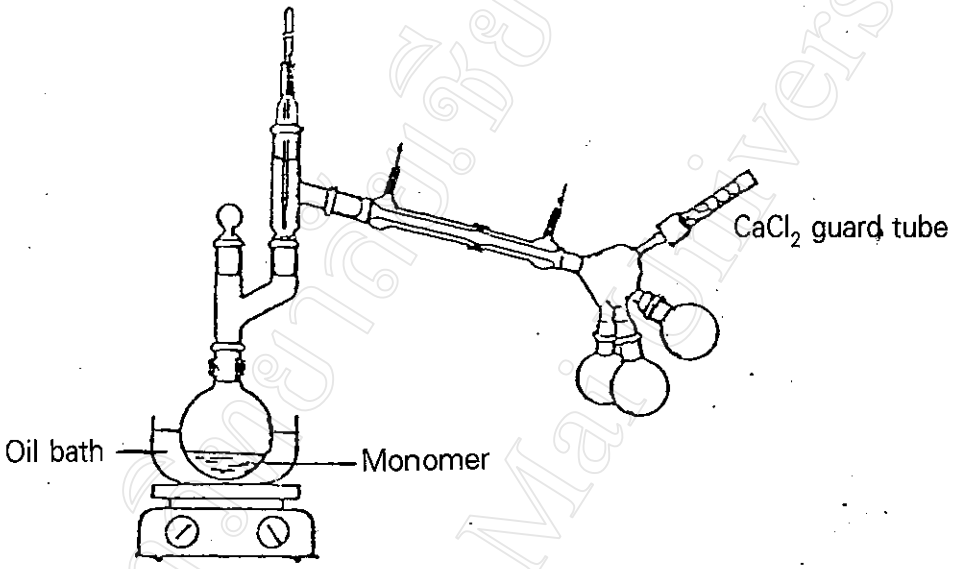


Figure 3.9 : Simple distillation apparatus used in the purification of methyl acrylate monomer.

The IR spectrum of the distilled methyl acrylate monomer is shown in Figure 3.10 and can be compared with the reference spectrum in Figure 3.11.

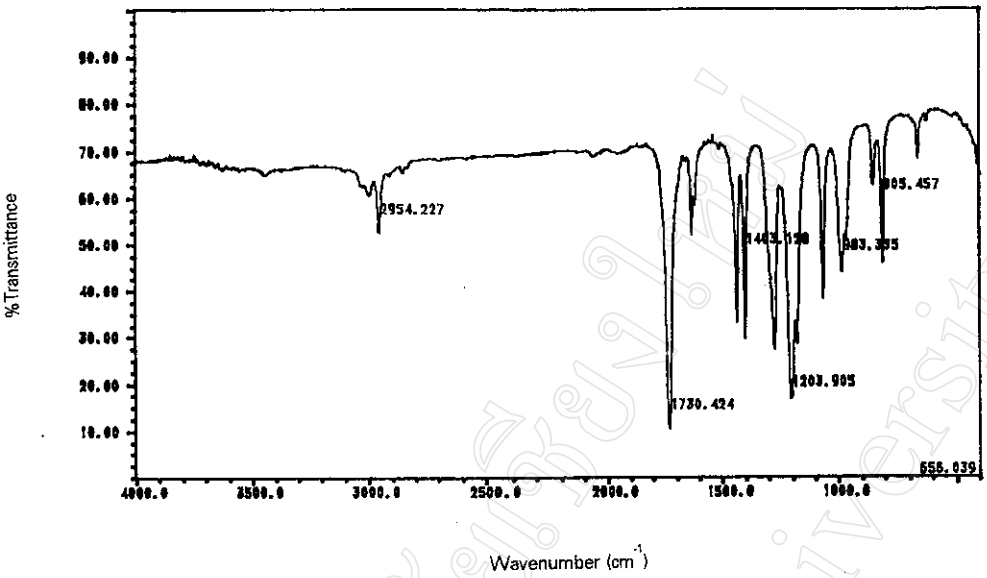


Figure 3.10 : Infrared spectrum of distilled methyl acrylate.

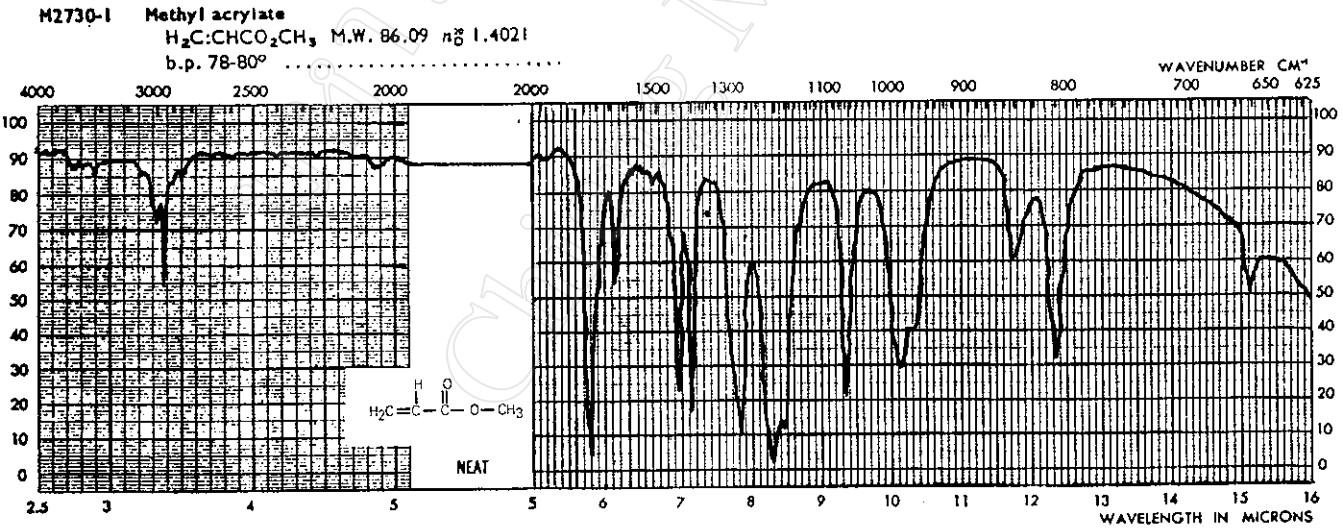
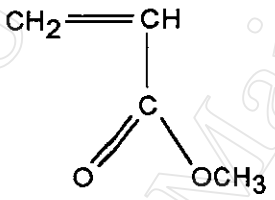


Figure 3.11 : Reference infrared spectrum of methyl acrylate [38].

Table 3.7 : Infrared absorption band assignments for methyl acrylate monomer.

Vibrational Assignments	Wavenumber (cm^{-1})
C-H stretching	2954
C=O stretching	1730
C=C stretching	1650
C-H bending , in CH_2	1450,1400
C-H bending , in CH_3	1300
C-O stretching, acyl-oxygen in C(=O)-O	1203
C-O stretching, alkyl-oxygen in CH_2-O	1080



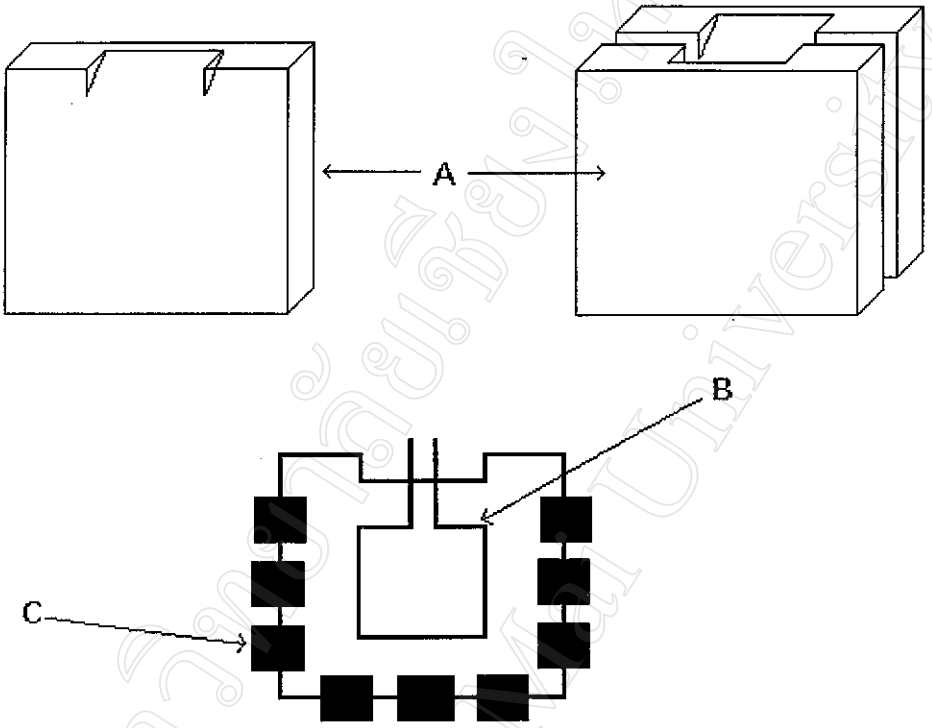
methyl acrylate

3.3 Bulk Polymerisation in the Form of Thin Sheets

3.3.1 Mould Design

The mould consisted of two square glass plates (15.0 cm x 15.0 cm), each lined on the inside with poly(ethylene terephthalate) (PET) film as release agent and

separated by a polytetrafluoroethylene (PTFE) covered wire gasket as spacer. The thickness of the spacer therefore determined the thickness of the final polymer sheet that was obtained. The two plates were held tightly together by clips with a small inlet at the top for injection of the polymerisation mixture. A diagram of the mould is shown in Figure 3.12.



A = glass plate with PET film liner

B = PTFE-coated wire gasket

C = clip

Figure 3.12 : Mould used for bulk polymerisation in the form of thin sheets.

3.3.2 Bulk Polymerisation / Copolymerisation Procedure [40]

Thin polymer sheets of uniform thickness were produced by *in situ* bulk polymerisation of the monomer mixtures in the mould described in section 3.3.1. The

monomers were mixed together with the benzoyl peroxide initiator (0.1 mol%) and ethylene glycol dimethacrylate crosslinking agent (1.0% w/w) at room temperature until a homogeneous clear solution was obtained. The rationale used in the choice of comonomer feed compositions was that the 2-hydroxyethyl methacrylate (HEMA) monomer is intended to be the major component in the resultant copolymer. The butyl acrylate (BA) and methyl acrylate (MA) comonomers are minor components intended to modify the properties of P(HEMA). The various comonomer feed compositions used are shown in Tables 3.8-3.9. Each mixture was deoxygenated with nitrogen before injection into the mould. The mould was then placed in an oven at 60.0°C for 3 days. The clips were removed and, after opening the mould, the thin sheet was separated from the PET film liners, then placed in deionized water to hydrate for at least a day. This was followed by postcuring at 90.0°C under vacuum to constant weight in order to remove the absorbed water and residual monomers. The thin sheets of polymer obtained were of uniform thickness (0.750 ± 0.100 mm), as determined by a micrometer at five different points.

Table 3.8 : Comonomer feed compositions of HEMA and BA used in copolymer synthesis.

Polymers	Comonomer Feed Compositions	
	HEMA (wt.%)	BA (wt.%)
P(HEMA)	100	0
P(HEMA-co-BA)/95:5	95	5
P(HEMA-co-BA)/90:10	90	10
P(HEMA-co-BA)/85:15	85	15
P(HEMA-co-BA)/80:20	80	20
PBA	0	100

Table 3.9 : Comonomer feed compositions of HEMA and MA used in copolymer synthesis.

Polymers	Comonomer Feed Compositions	
	HEMA (wt.%)	BA (wt.%)
P(HEMA)	100	0
P(HEMA-co-MA)/95:5	95	5
P(HEMA-co-MA)/90:10	90	10
P(HEMA-co-MA)/85:15	85	15
P(HEMA-co-MA)/80:20	80	20
PMA	0	100

3.4 Polymer Characterisation

3.4.1 Polymer Properties Relevant to Intended Application

Some properties of the thin sheet polymers obtained which are relevant to their intended use as temporary skin substitutes are shown in Table 3.10 - 3.11.

Table 3.10 : Some properties of the dry polymer or copolymer sheets relevant to their use as temporary skin substitutes.

Polymer Properties	P(HEMA)	PBA	PMA	P(HEMA-co-BA)	P(HEMA-co-MA)
Colour	colourless	colourless	colourless	colourless	colourless
Transparency	transparent	transparent	transparent	transparent	transparent
Flexibility	fairly stiff	flexible	flexible	fairly stiff	fairly stiff
Adherence to the skin	non-adhesive	adhesive	adhesive	non-adhesive	non-adhesive

Table 3.11 : Some properties of the hydrated polymer or copolymer sheets relevant to their use as temporary skin substitutes.

Polymer Properties*	P(HEMA)	PBA	PMA	P(HEMA-co-BA)	P(HEMA-co-MA)
Colour	colourless	colourless	colourless	colourless	colourless
Transparency	transparent	transparent	transparent	transparent	transparent
Flexibility	flexible	more flexible than P(HEMA)	more flexible than PBA	more flexible than P(HEMA)	more flexible than P(HEMA)
Adherence to the skin	slightly adhesive	more adhesive than P(HEMA)	more adhesive than PBA	more adhesive than P(HEMA)	more adhesive than P(HEMA)

* The polymer or copolymer sheets were hydrated in deionized water to equilibrium at room temperature.

3.4.2 Solubility [41]

The molecules of a solid polymer are held together by van der Waal's forces and, in some cases, by hydrogen bonding or the interaction of polar groups. Forces between polymer molecules will increase with molecular size and, in the case of linear molecules, with chain length. Because of the increase in attractive forces between molecules with increasing chain length, the dissolving of linear polymers will be more

difficult than the solution of chemically similar smaller molecules. There are two other factors which affect the solubility of polymer molecules. These are the type of packing of the chains and the rigidity of the molecules. The type of packing determines the fraction of the theoretical maximum number of secondary bonds that can exist between chains. Relatively noncrystalline material is not regularly arranged and so has comparatively loose packing and few bonds between chains. The solvent can penetrate easily into such a material and can separate the chains at many points. In contrast, tightly packed, more crystalline polymers resist such penetration and must be dissolved gradually, beginning at the outer surface of the crystallites.

Two compounds having similar types of packing and the same type of attractive forces between molecules may also vary in solubility because of a difference in the rigidity of the chains. A very flexible high polymer can be dissolved by breaking each intermolecular secondary bond in turn, the equivalent of prying the molecules apart at one point. A completely rigid material cannot be as easily separated, since all the bonds joining one chain to the other must be broken simultaneously, in a manner resembling the pulling apart of two rigid bars that have been glued together.

The effect of the magnitude of the forces between chains, as determined by functional groups, is also important. This effect may be more responsible for the solubility behavior than any other factor. The extremes of intermolecular forces may be illustrated by comparing a linear polymer that is very loosely held together in the solid state with a material in which a number of crosslinks have been established by chemical bonds. If the polymer consists of a crosslinked or continuous network structure, the action of even good solvents is limited to swelling. The amount of liquid absorbed will reach a limit beyond which no further swelling occurs and a rather well-defined swelling equilibrium state is established. The swelling may be regarded as the expansion of the network structure by the solvent molecules up to the point where the elastic force in the

network counterbalances the ability of the solvent to pry the chains apart. The greater the number of crosslinks, the less the polymer will swell in contact with the solvent. In the case of a moderately crosslinked structure, swelling may exceed a fiftyfold increase in volume, whereas a highly crosslinked structure may be only slightly affected.

In this work, the following procedure was used for the rapid determination of polymer solubility. A small piece of the uncrosslinked polymer was mixed with 5 ml of solvent in a test tube and stirred together thoroughly. If no sign of solubility occurred at room temperature, the mixture was heated gently at or just below the boiling point of the solvent. If the polymer dissolved, the solution was allowed to cool to see if the polymer remained in solution or precipitated. If the polymer was swollen by the solvent but was not dissolved, other various solvents were checked in the same way. The solubility test results for the uncrosslinked homopolymers are shown in Table 3.12 below.

Table 3.12 : Solubility test results for the uncrosslinked homopolymers.

Polymer / Solvent	P(HEMA)	PBA	PMA
Ethanol	SW	X	X
Methanol	X	X	X
Acetone	X	X	X
Chloroform	X	X	X
Toluene	X	X	√
Dimethyl sulfoxide	SW	√	√
Benzene : Ethanol (1:1)	SW	X	X
Water	SW	X	X

Notations : X = insoluble, SW = swellable, √ = soluble at room temp.

3.4.3 Infrared Spectroscopy [42]

Infrared spectroscopic techniques are widely used in both qualitative and quantitative analysis. They are particularly valuable in the qualitative analysis of polymers and compositions containing polymers, since the characterisation of these materials is often difficult by the more usual chemical and physical methods. For qualitative analysis, it is useful to consider the infrared spectrum to be made up of absorption bands which arise from the presence, in the substance examined, of pairs or small groups of atoms. In this research, a Nicolet FT-IR 510 Infrared Spectrometer was used for the qualitative analysis of the homopolymers and copolymers. The samples for FT-IR analysis were prepared in the form of KBr discs.

The infrared spectra of the homopolymers and copolymers, together with their reference spectra where available, are shown in Figures 3.13 - 3.26. The major vibrational peaks are listed in Tables 3.13 - 3.15.

Table 3.13 : Infrared absorption band assignments for crosslinked P(HEMA).

Vibrational Assignments	Wavenumber (cm^{-1})
O-H stretching	3600-3400
C-H stretching	2950
C=O stretching	1740
C-H bending , in CH_2	1490,1450
C-H bending , in CH_3	1400
C-O stretching, acyl-oxygen in C(=O)-O	1300
C-O stretching, alkyl-oxygen in CH_2-O	1180

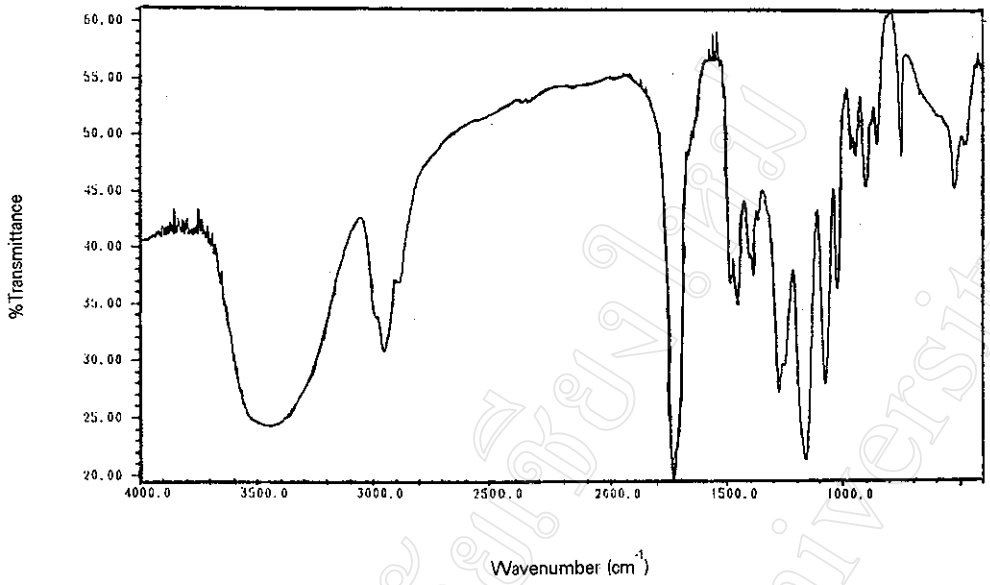


Figure 3.13 : Infrared spectrum of crosslinked P(HEMA).

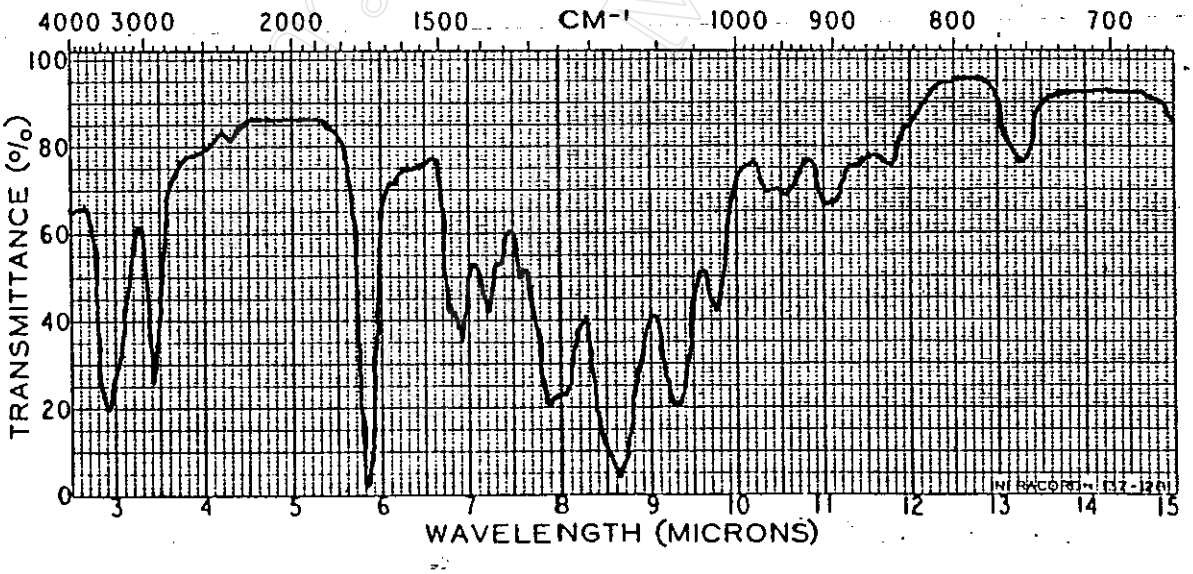


Figure 3.14 : Reference infrared spectrum of P(HEMA) [42].

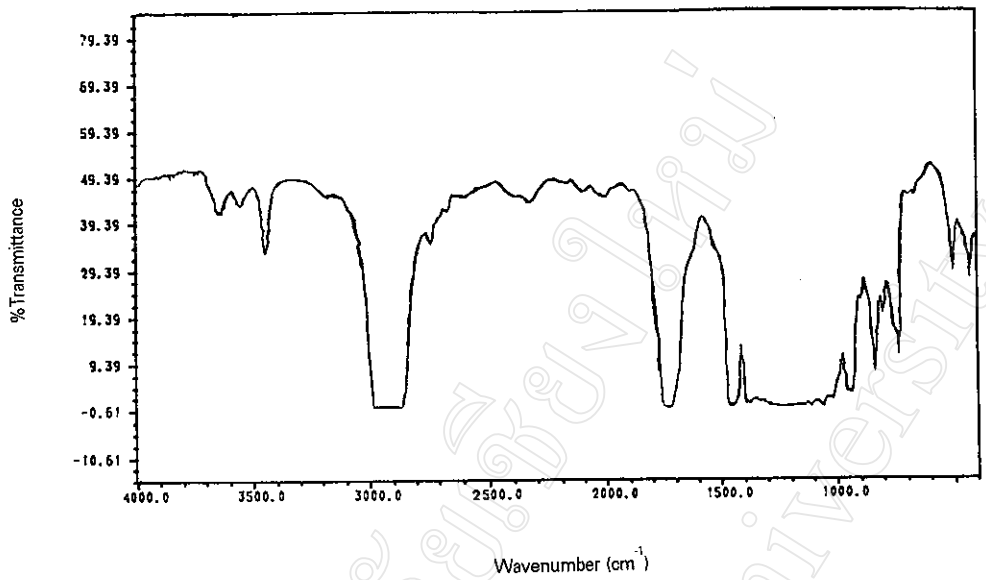


Figure 3.15 : Infrared spectrum of crosslinked PBA.

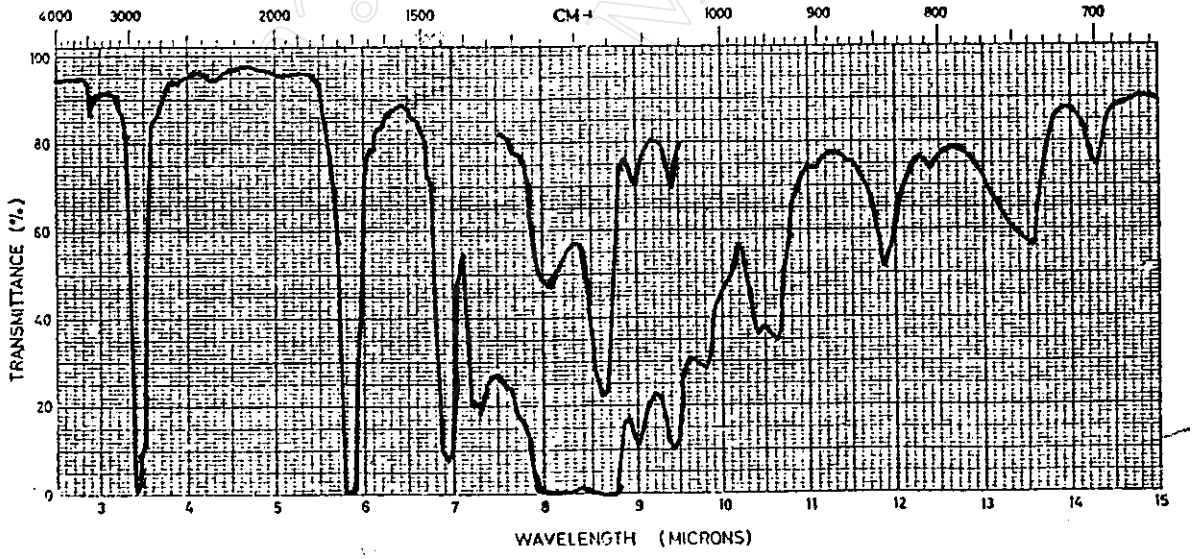


Figure 3.16 : Reference infrared spectrum of PBA [42].

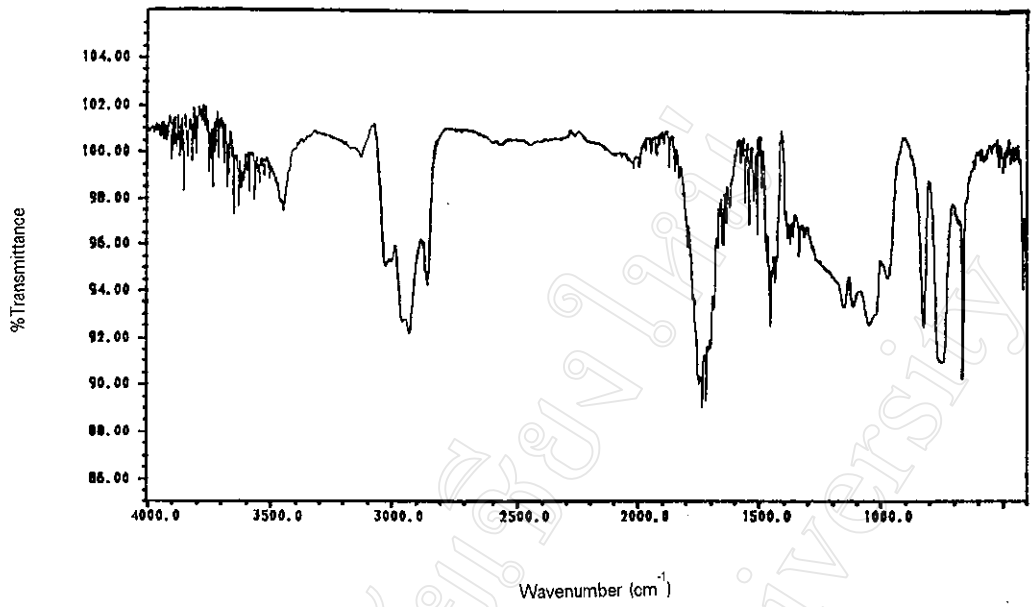


Figure 3.17 : Infrared spectrum of crosslinked PMA.

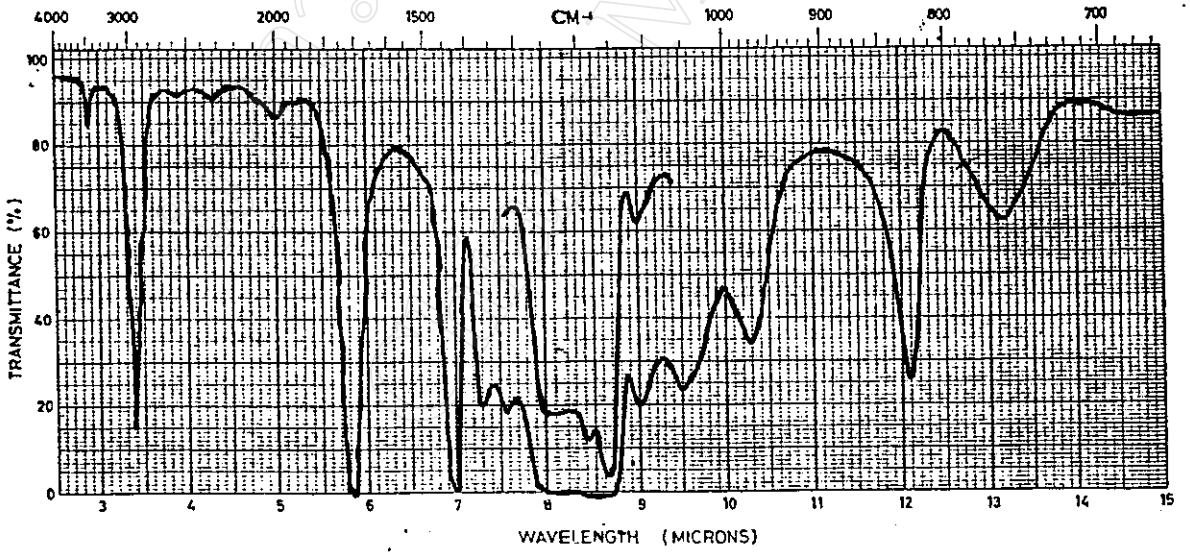


Figure 3.18 : Reference infrared spectrum of PMA [42].

Table 3.14 : Infrared absorption band assignments for crosslinked PBA.

Vibrational Assignments	Wavenumber (cm^{-1})
C-H stretching	2880-2860
C=O stretching	1740
C-H bending , in CH_2	1460
C-O stretching, acyl-oxygen in C(=O)-O	1200-1300
C-O stretching, alkyl-oxygen in CH_2-O	980

Table 3.15 : Infrared absorption band assignments for crosslinked PMA.

Vibrational Assignments	Wavenumber (cm^{-1})
C-H stretching	2940
C=O stretching	1750
C-H bending , in CH_2	1460
C-H bending , in CH_3	1350
C-O stretching, acyl-oxygen in C(=O)-O	1130-1180
C-O stretching, alkyl-oxygen in CH_2-O	1050

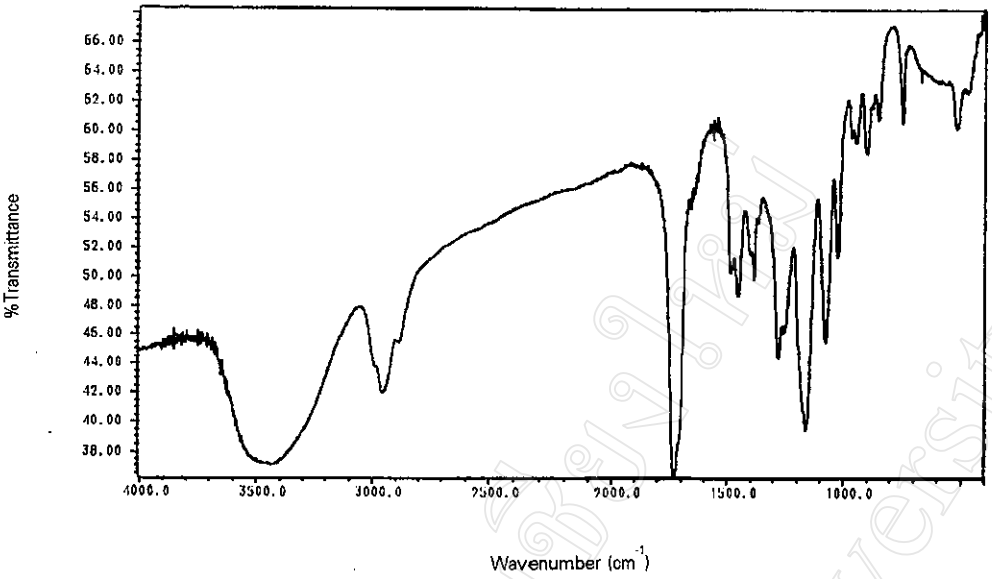


Figure 3.19 : Infrared spectrum of crosslinked P(HEMA-co-BA)/95:5.

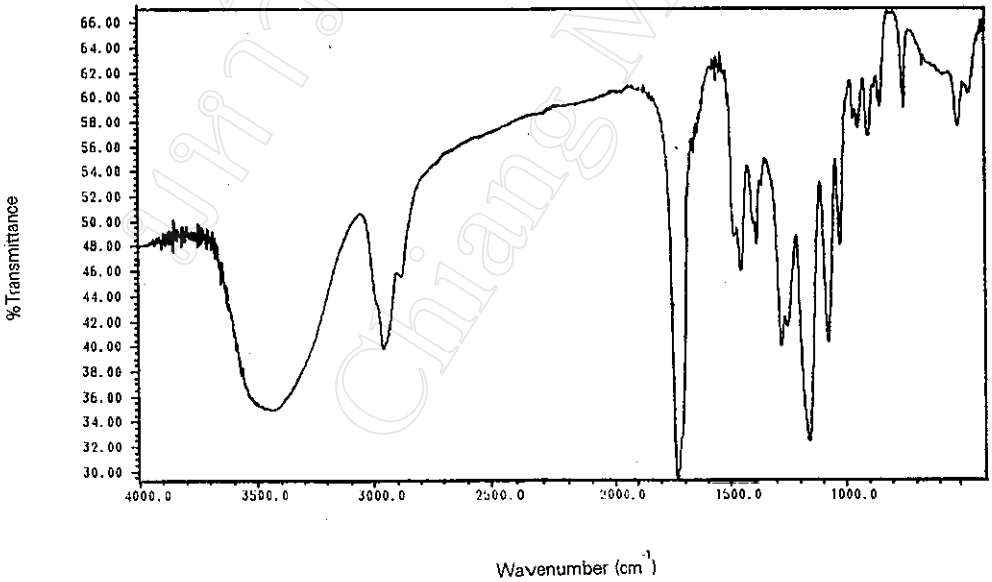


Figure 3.20 : Infrared spectrum of crosslinked P(HEMA-co-BA)/90:10.

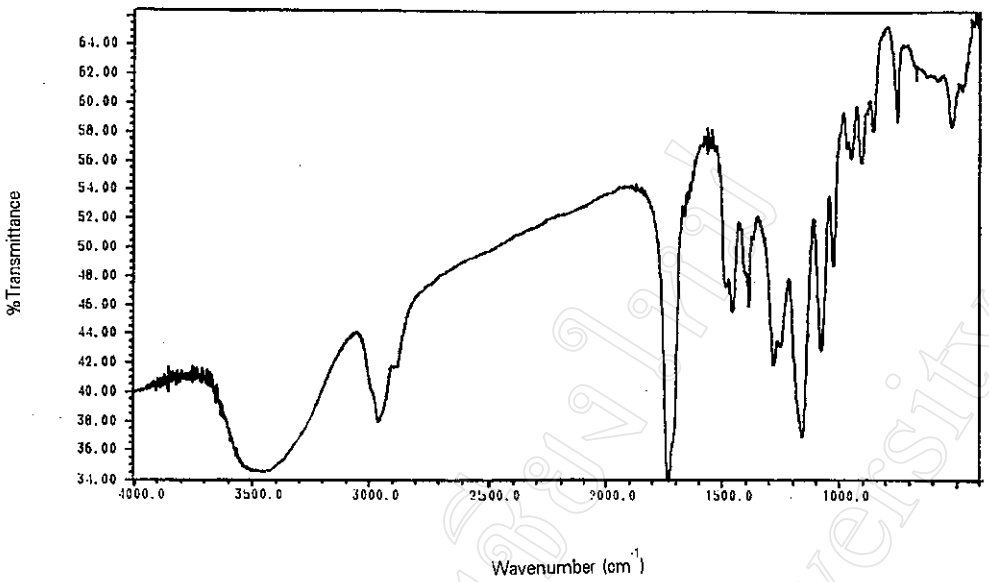


Figure 3.21 : Infrared spectrum of crosslinked P(HEMA-co-BA)/85:15.

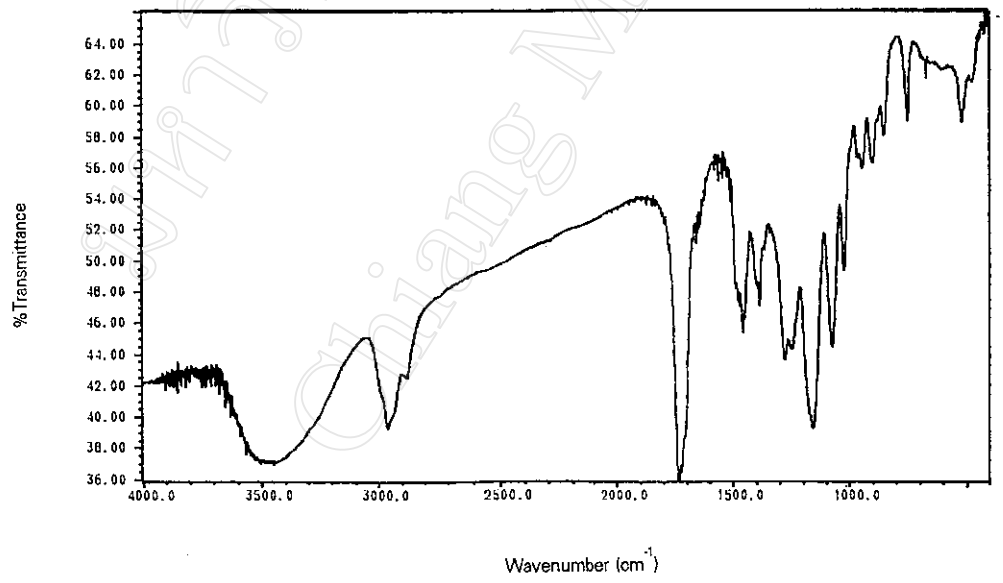


Figure 3.22 : Infrared spectrum of crosslinked P(HEMA-co-BA)/80:20.

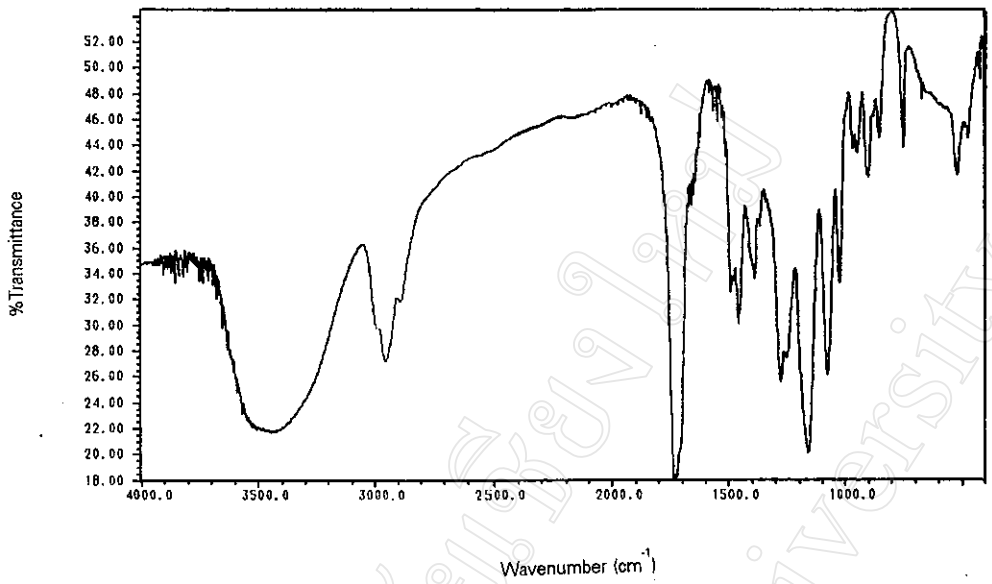


Figure 3.23 : Infrared spectrum of crosslinked P(HEMA-co-MA)/95:5.

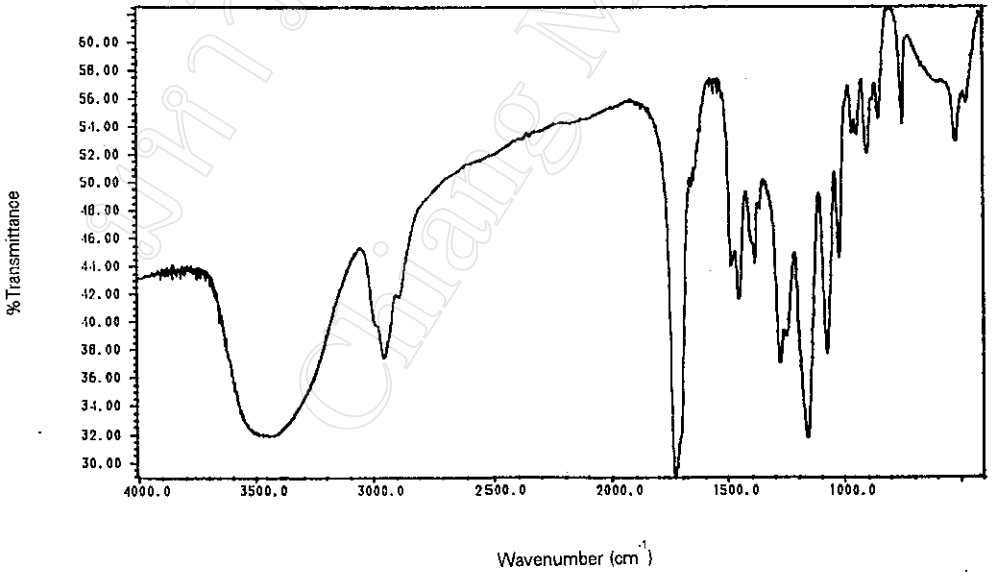


Figure 3.24 : Infrared spectrum of crosslinked P(HEMA-co-MA)/90:10.

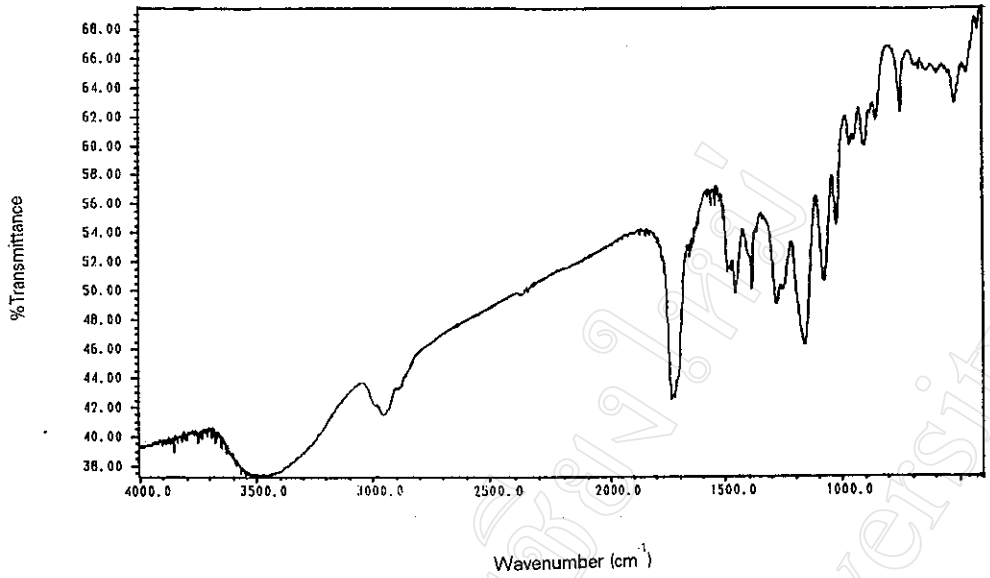


Figure 3.25 : Infrared spectrum of crosslinked P(HEMA-co-MA)/85:15.

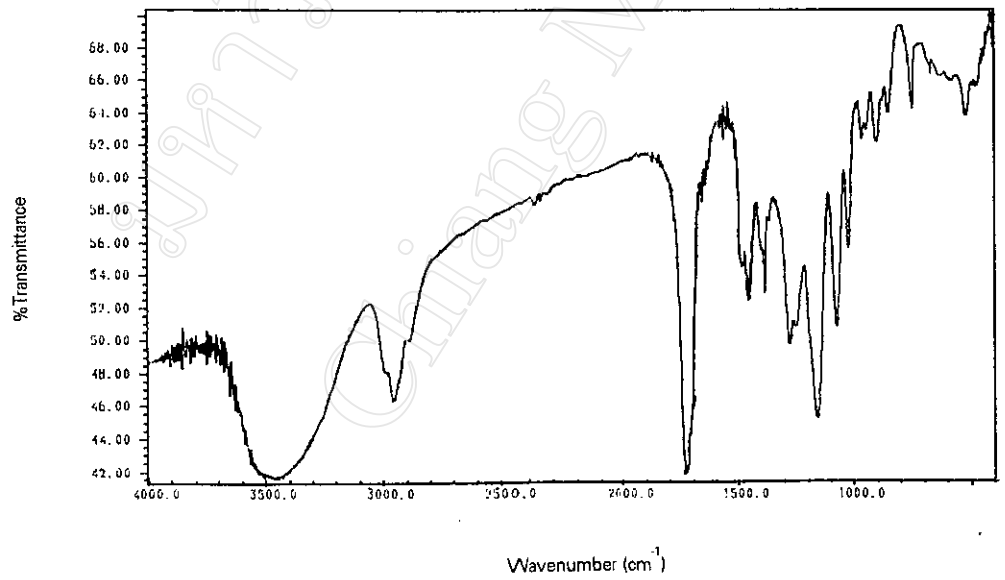


Figure 3.26 : Infrared spectrum of crosslinked P(HEMA-co-MA)/80:20.

As expected, the infrared spectra of the P(HEMA-co-BA) and P(HEMA-co-MA) copolymers are very similar to that of P(HEMA) since the BA and MA units contain the same functional groups as the HEMA units except for the -OH group. Consequently, this IR technique is not really suitable for quantitative compositional analysis of the copolymers studied in this work; it can only be used for their qualitative characterisation.

3.4.4 Elemental Analysis [43]

The elemental analysis technique is useful in both homopolymer and copolymer characterisation. Since polymers are usually composed of the elements carbon, hydrogen, nitrogen, oxygen and sulphur, the percentages of which can be accurately determined by elemental analysis, the relative amounts of each monomer in a copolymer can be calculated. In this research, a Perkin-Elmer PE 2400 Series II CHNS/O Analyzer was used to determine the carbon, hydrogen and oxygen contents in the homopolymers and copolymers.

In the CHN operating mode, the PE 2400 Series II CHNS/O Analyzer uses a combustion method to convert the sample elements to simple gases (CO_2, H_2O, and N_2). The sample is first oxidized in a pure oxygen environment using classical reagents. Products produced in the combusion zone include CO_2, H_2O, and N_2. Other elements, such as halogens and sulfur, are removed by scrubbing reagents in the combustion zone. The resulting gases are homogenized and controlled to exact conditions of pressure, temperature, and volume. The homogenized gases are allowed to de-pressurize through a column where they are separated in a stepwise steady-state manner and detected as a function of their thermal conductivites.

In the oxygen operating mode, the PE 2400 Series II CHNS/O Analyzer performs oxygen analysis. The sample is pyrolyzed in a helium/hydrogen environment at 1000°C over platinized carbon where the pyrolyzed oxygen products of reaction are converted to carbon monoxide. The carbon monoxide and other gases pass through a scrubber trap where acid gases and water are removed. As in the CHN mode, the resulting gases are homogenized and controlled to exact conditions of pressure, temperature, and volume before being allowed to de-pressurize through a column where they are separated and then detected. A helium/hydrogen (or argon/hydrogen) carrier gas mixture is used in this procedure to enhance the conversion of oxygen to carbon monoxide.

A summary of the results obtained from elemental analysis of the polymers synthesized in this research are given in Tables 3.16 - 3.17. In the case of the homopolymers, their elemental compositions are exactly known and so their calculated % compositions from the CHNO data can be compared with the corresponding theoretical values. However, in the case of the copolymers, their compositions can only be assumed to be approximately equal to their respective initial comonomer feeds. Nevertheless, this is a reasonable assumption since the bulk copolymerisations were allowed to proceed slowly over a long period of time(3 days) towards 100% conversion. As the results in both Tables 3.16 and 3.17 show, the experimentally found elemental compositions agree closely with their corresponding theoretical values.

Table 3.16 : Elemental analysis results for the homopolymers.

Homopolymer	Carbon (wt %)		Hydrogen (wt %)		Oxygen (wt %)	
	Theoretical	Found	Theoretical	Found	Theoretical	Found
Uncrosslinked P(HEMA)	55.4	51.97	7.7	9.37	36.9	37.73
Crosslinked P(HEMA)	55.4	52.15	7.7	9.44	36.9	37.56
Uncrosslinked PBA	65.6	65.26	9.4	10.06	25.0	24.56
Crosslinked PBA	65.5	65.53	9.4	10.37	25.1	24.71
Uncrosslinked PMA	55.8	55.61	7.0	7.62	37.2	37.62
Crosslinked PMA	55.9	55.80	7.0	7.43	37.1	36.24

Table 3.17 : Elemental analysis results for the crosslinked copolymer.

Copolymer (crosslinked)	Carbon (wt %)		Hydrogen (wt %)		Oxygen (wt %)	
	Theoretical	Found	Theoretical	Found	Theoretical	Found
P(HEMA-co-BA) 95:5	55.9	53.20	7.8	8.35	36.3	36.77
P(HEMA-co-BA) 90:10	56.4	53.96	7.9	8.45	35.7	36.59
P(HEMA-co-BA) 85:15	56.9	54.01	8.0	9.37	35.1	36.36
P(HEMA-co-BA) 80:20	57.5	55.08	8.0	8.00	34.5	35.28
P(HEMA-co-MA) 95:5	55.5	52.40	7.6	8.32	36.9	37.73
P(HEMA-co-MA) 90:10	55.4	52.18	7.7	7.98	36.9	37.64
P(HEMA-co-MA) 85:15	55.5	52.72	7.6	8.06	36.9	37.81
P(HEMA-co-MA) 80:20	55.6	52.93	7.6	8.80	36.8	37.42

3.5 Thermal Analysis [44]

Thermal analysis is defined by the ICTA (International Confederation for Thermal Analysis) as a "term covering a group of techniques in which a physical property of a substance and/or its reaction product(s) is measured as a function of temperature". The major techniques of thermal analysis can readily be grouped into three headings. differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermogravimetry (TG). In this research project, DSC and TG were the techniques employed for polymer characterisation.

3.5.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measures the amount of energy (heat) absorbed or released by a sample as it is heated, cooled or held isothermally at a constant temperature. DSC curves reflect changes in the energy of the system under investigation, changes that may be chemical or physical in origin. This technique is therefore particularly useful for polymers because polymerisation or structural changes are almost invariably accompanied by energetic effects. Hence, crystallisation and melting, curing and other reactions, and the glass transition all show characteristic DSC features.

The DSC experiments in this project were carried out using a Perkin-Elmer DSC7 Differential Scanning Calorimeter. Each sample in the shape of a disc weighing about 3-5 mg was vacuum dried at 60.0°C to constant weight in order to remove any absorbed moisture. The samples were then heated in sealed aluminium pans at a rate of 10.0°C/min under a flowing nitrogen atmosphere. The DSC curve is obtained by calculating the heat flow to or from the sample from the temperature difference measured between the sample pan and a reference pan. The heat effects involved in the phase transitions of

the samples are calculated from the areas under the curve. The DSC curves of the homopolymers and copolymers are shown in Figures 3.27 - 3.40 and the glass transition temperatures, T_g, where evident, compared in Table 3.18. The tangent line constructions used to locate the T_g values in the DSC curves are in accordance with generally accepted principles of DSC data analysis.

The appearance of a T_g transition in the DSC curve varies from sample to sample, depending upon both crosslinking and chemical composition. The T_g becomes less distinct with crosslinking, due to the restriction in molecular motion, and also with increasing MA/BA content in the copolymer. These effects will be discussed in more detail in the following chapter.

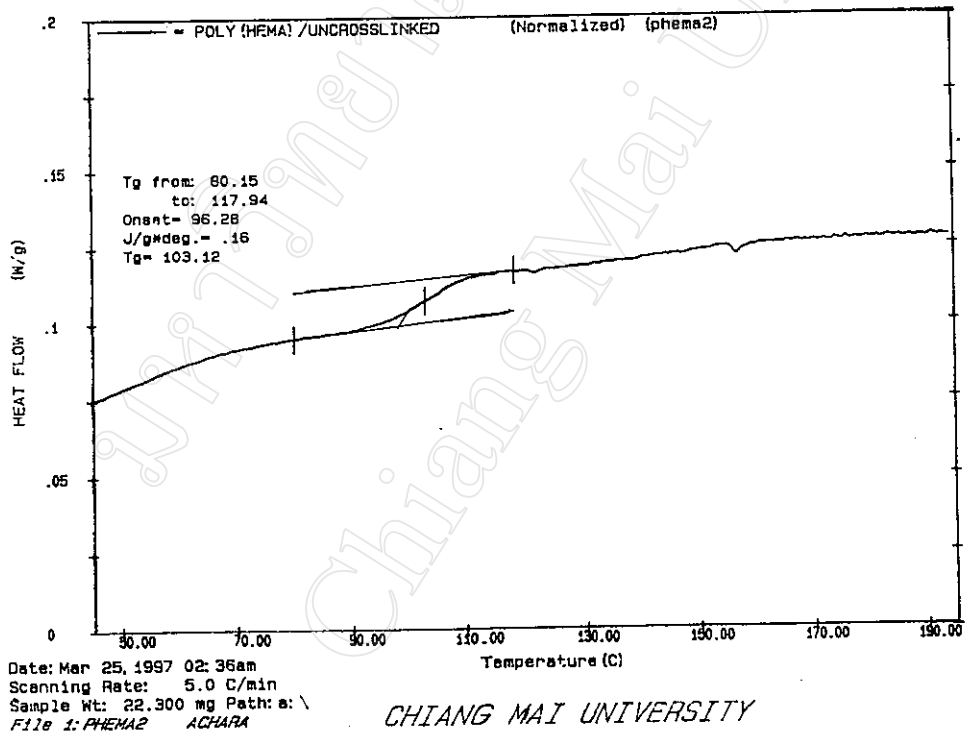


Figure 3.27 : DSC thermogram of uncrosslinked P(HEMA).

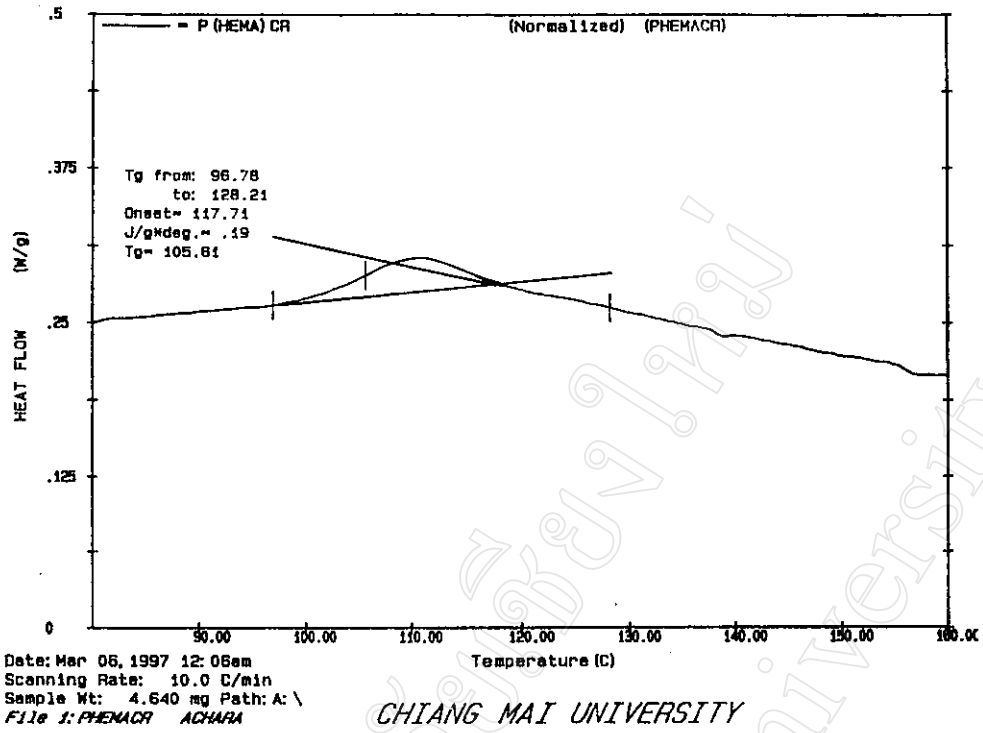


Figure 3.28 : DSC thermogram of crosslinked P(HEMA).

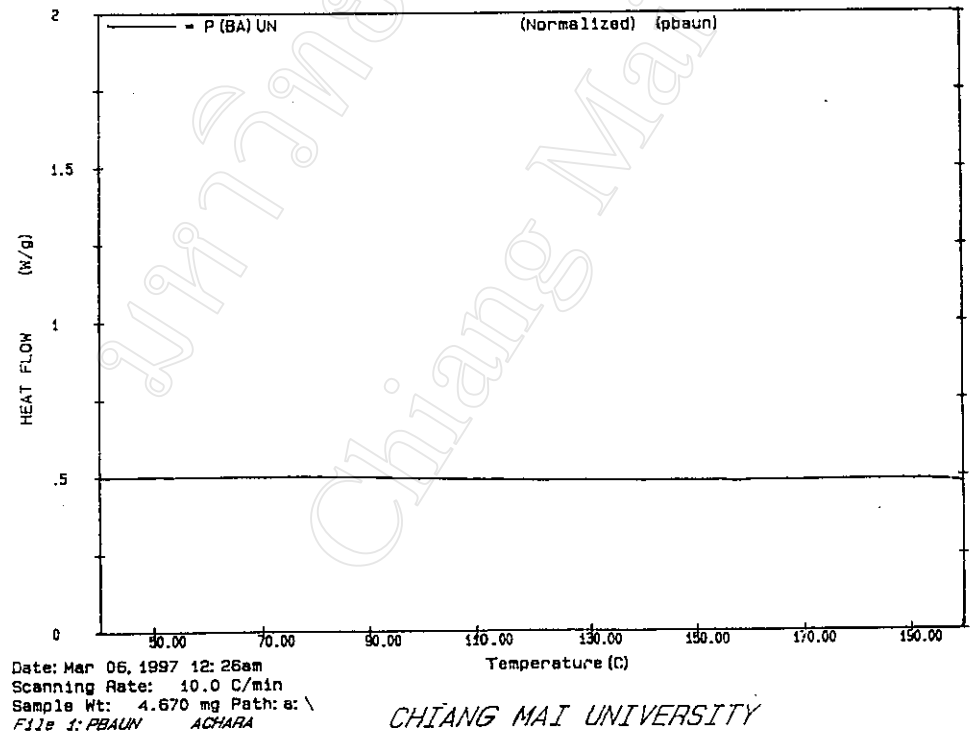


Figure 3.29 : DSC thermogram of uncrosslinked PBA.

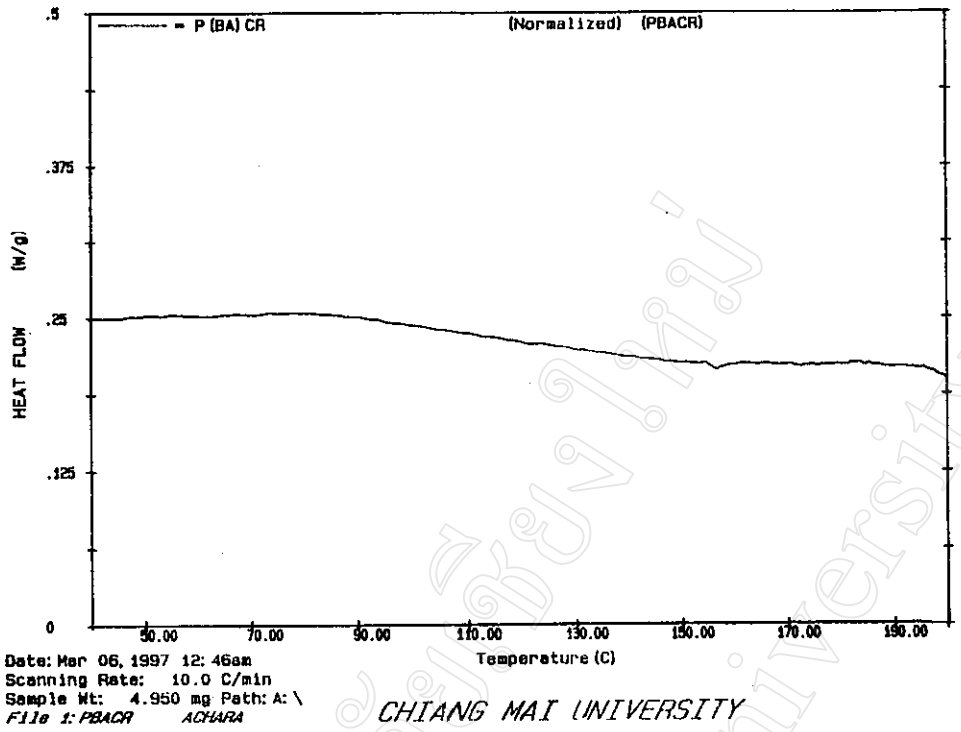


Figure 3.30 : DSC thermogram of crosslinked PBA.

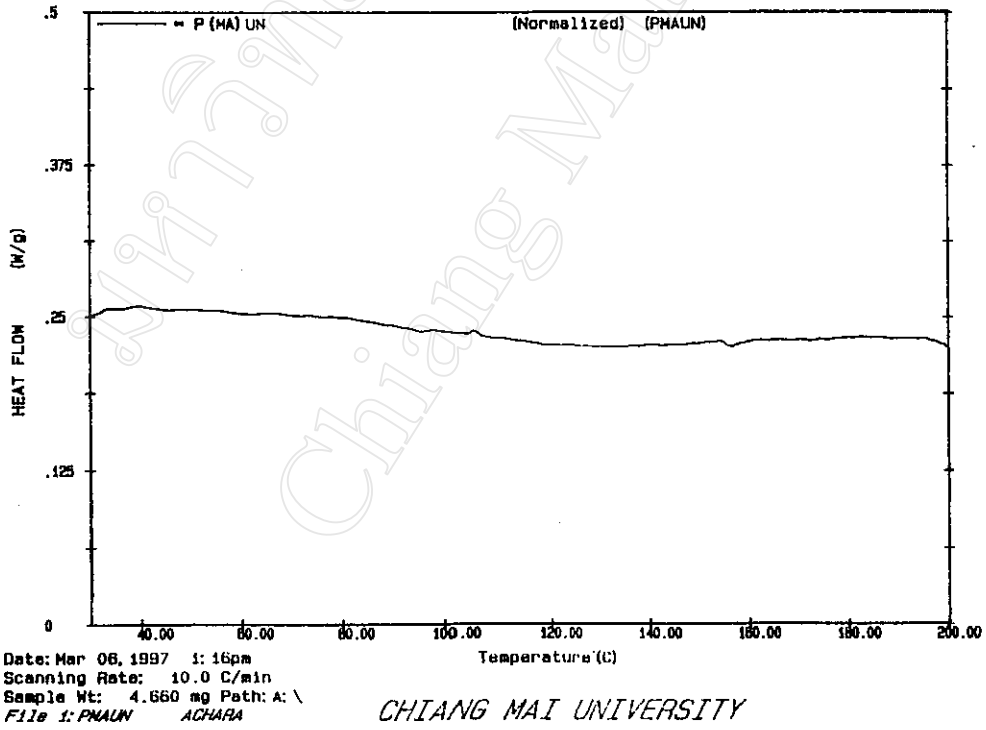


Figure 3.31 : DSC thermogram of uncrosslinked PMA.

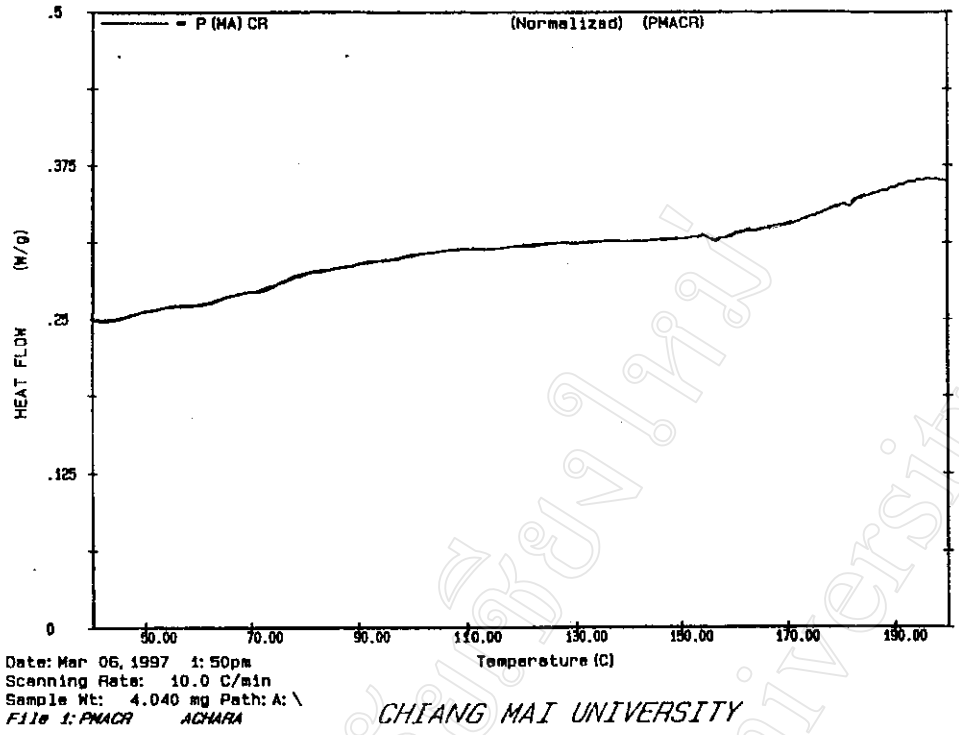


Figure 3.32 : DSC thermogram of crosslinked PMA.

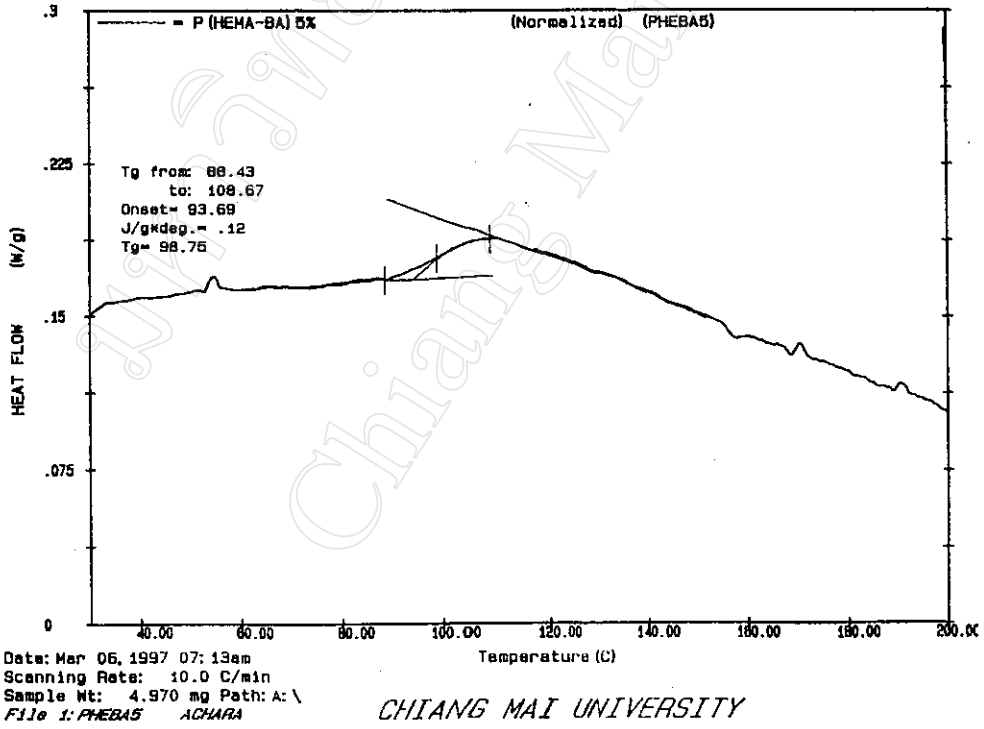


Figure 3.33 : DSC thermogram of crosslinked P(HEMA-co-BA)/95:5.

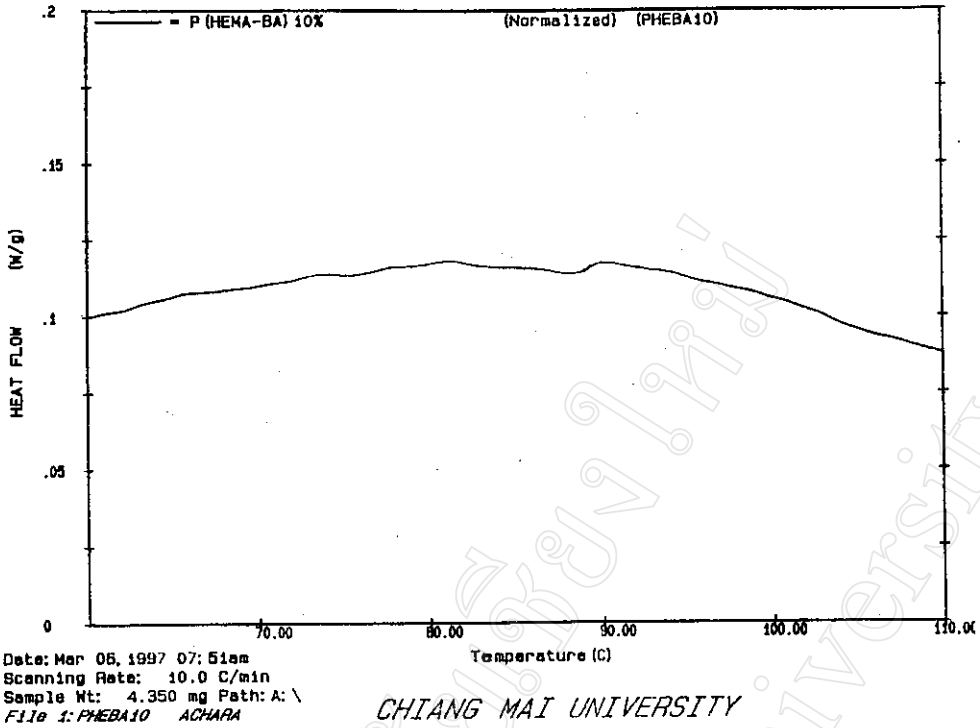


Figure 3.34 : DSC thermogram of crosslinked P(HEMA-co-BA)/90:10.

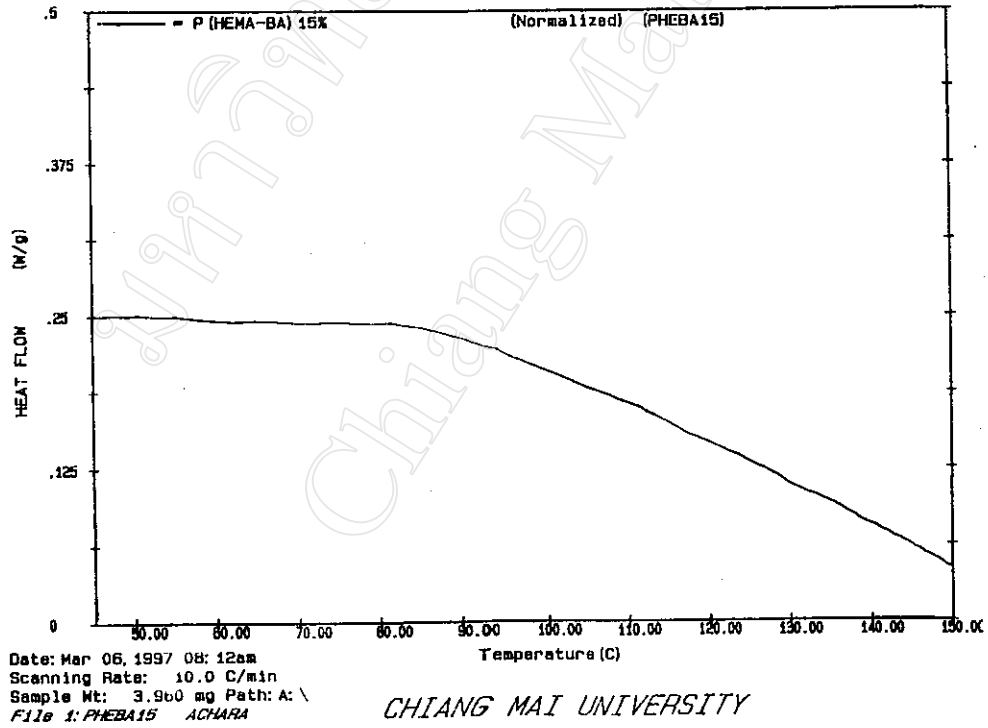


Figure 3.35 : DSC thermogram of crosslinked P(HEMA-co-BA)/85:15.

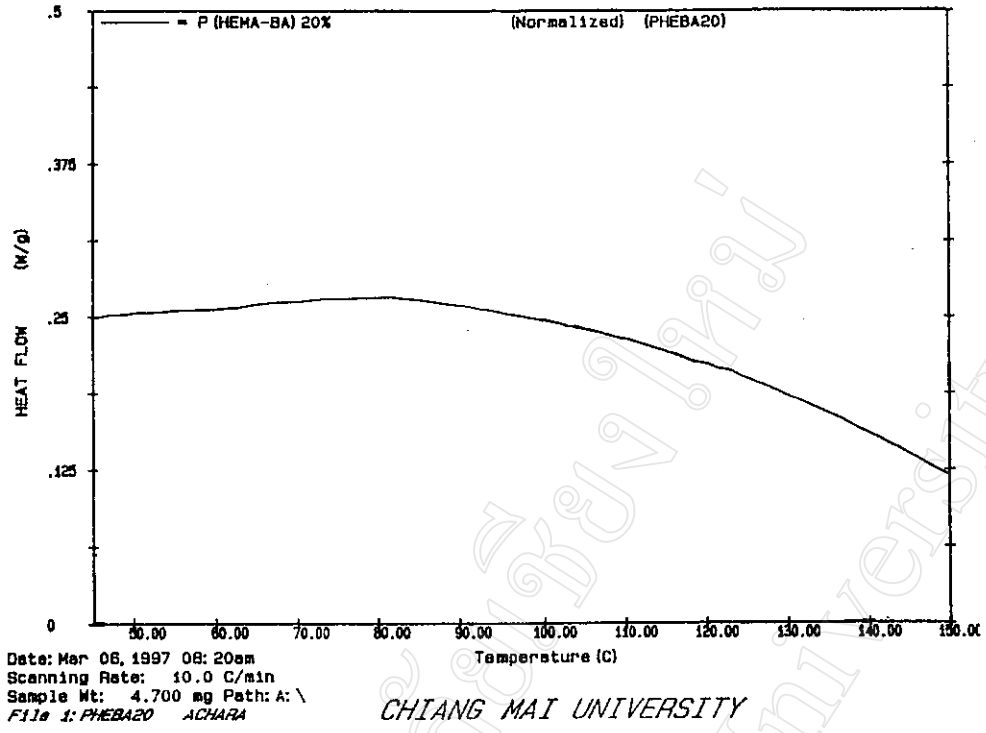


Figure 3.36 : DSC thermogram of crosslinked P(HEMA-co-BA)/80:20.

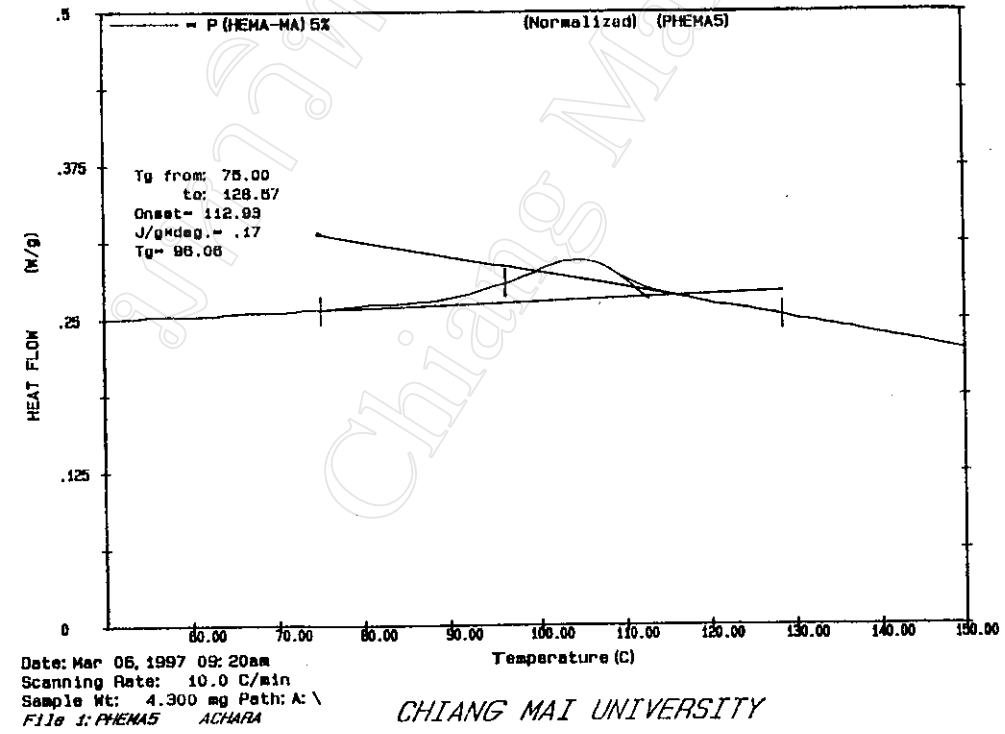


Figure 3.37 : DSC thermogram of crosslinked P(HEMA-co-MA)/95:5.

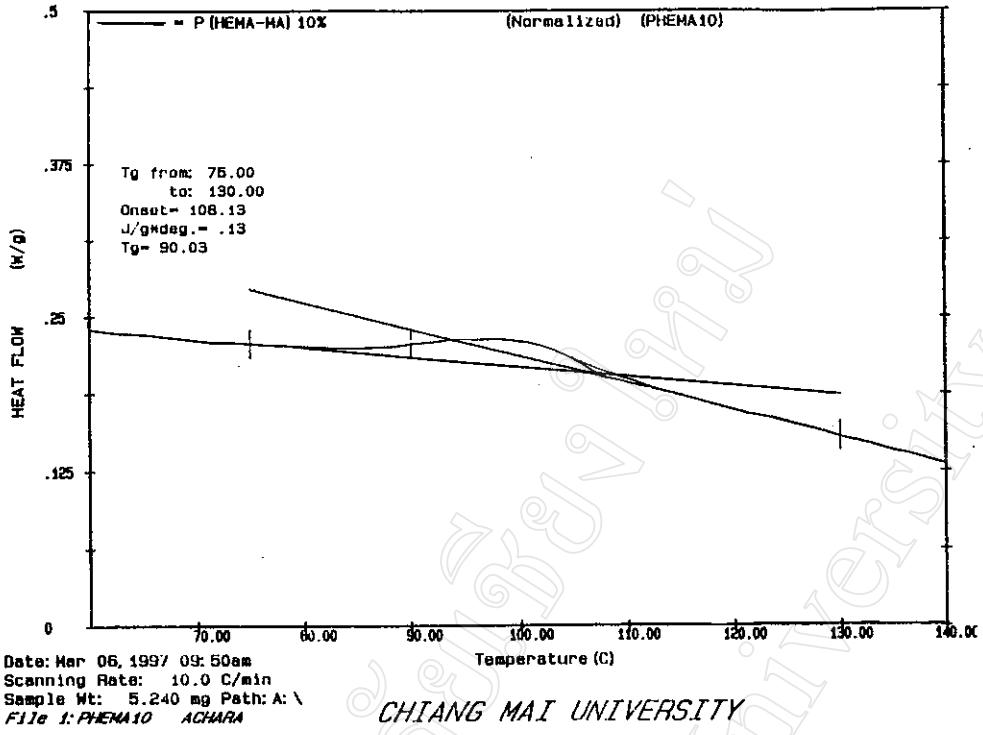


Figure 3.38 : DSC thermogram of crosslinked P(HEMA-co-MA)/90:10.

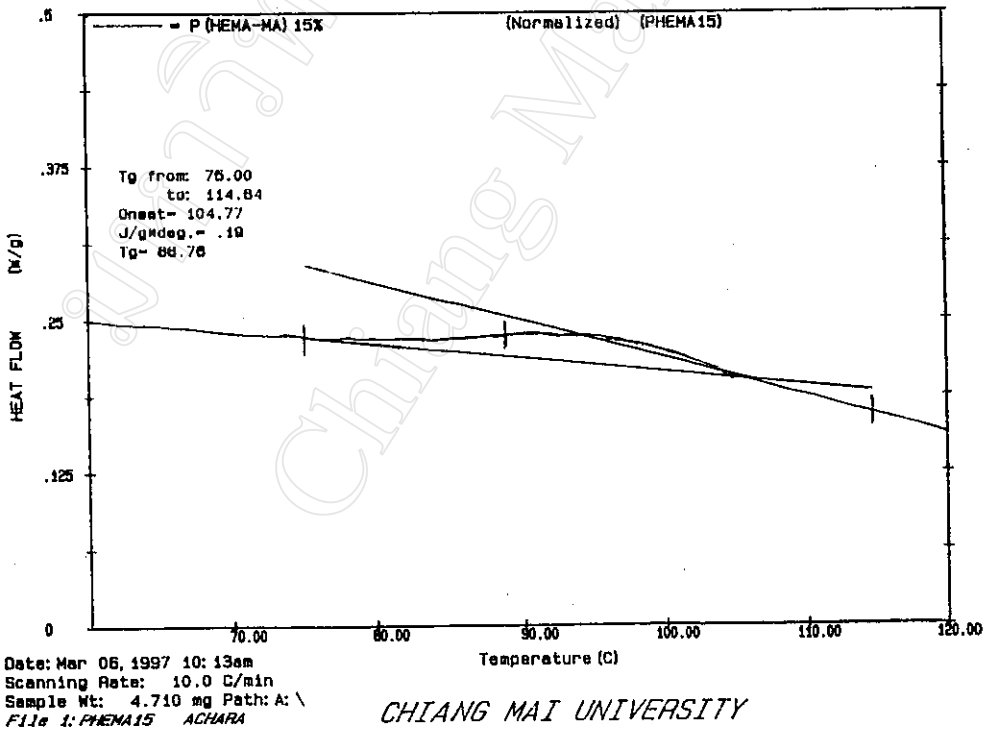


Figure 3.39 : DSC thermogram of crosslinked P(HEMA-co-MA)/85:15.

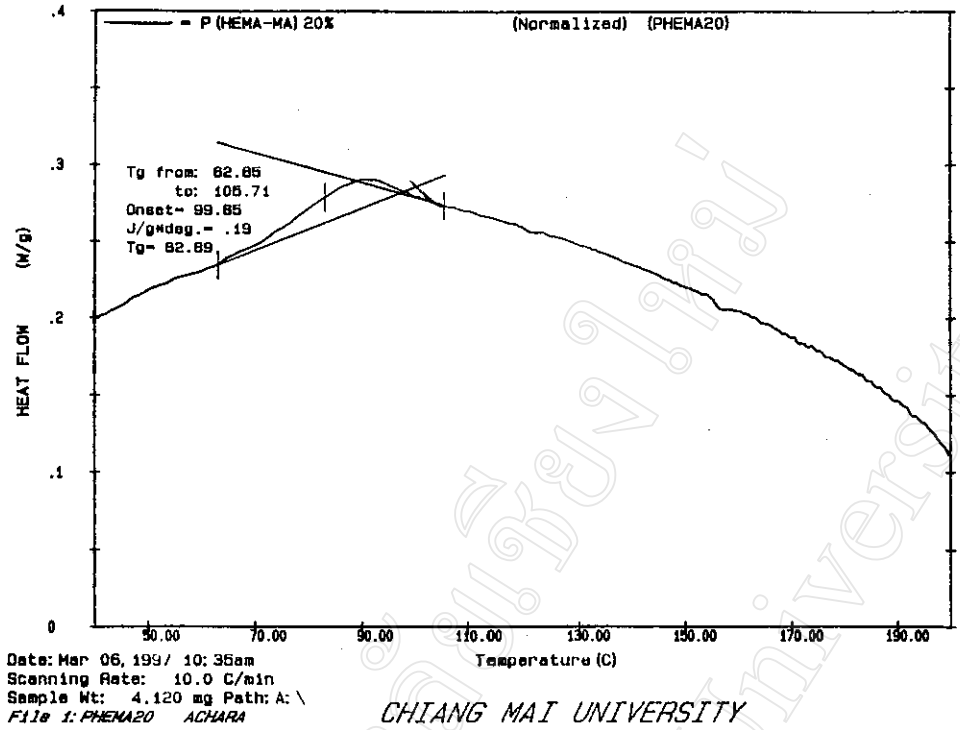


Figure 3.40 : DSC thermogram of crosslinked P(HEMA-co-MA)/80:20.

Table 3.18 : Comparison of the glass transition temperatures, T_g, obtained from the DSC curves of the homopolymers and copolymers.

Homopolymer or Copolymer	Observed T_g (°C)	Reference T_g (°C)
uncrosslinked P(HEMA)	103	104[(a)]
crosslinked P(HEMA)	106	-
uncrosslinked PBA	-	-54[(a)]
crosslinked PBA	-	-
uncrosslinked PMA	-	10[(a)]
crosslinked PMA	-	-
crosslinked P(HEMA-co-BA)/95:5	99	91[(b)]
crosslinked P(HEMA-co-BA)/90:10	-	79[(b)]
crosslinked P(HEMA-co-BA)/85:15	-	67[(b)]
crosslinked P(HEMA-co-BA)/80:20	-	56[(b)]
crosslinked P(HEMA-co-MA)/95:5	96	98[(b)]
crosslinked P(HEMA-co-MA)/90:10	90	92[(b)]
crosslinked P(HEMA-co-MA)/85:15	89	86[(b)]
crosslinked P(HEMA-co-MA)/80:20	83	81[(b)]

(a) Literature values [45]

(b) Calculated values from the Fox Equation (for uncrosslinked random copolymers of A and B)

$$\frac{1}{T_{g\,AB}} = \frac{w_A}{T_{g\,A}} + \frac{w_B}{T_{g\,B}}$$

w_A, w_B = respective weight fractions, T_g values in °K

3.5.2 Thermogravimetry

Thermogravimetry, TG, measures the change in mass of a sample as it is heated, cooled or held isothermally at a constant temperature. This technique is used widely as a means of assessing the thermal stability of polymeric materials and, as such, it can provide valuable technical information. However, it must be borne in mind that the conclusions drawn with regard to stability are only relevant within the context of loss-of-weight of the sample, There are reactions which can take place on heating a polymer and which alter drastically the physical properties of the material without an observed change in weight.

In this work, the TG experiments were carried out using a Perkin-Elmer TGA7 Thermogravimetric Analyzer. Since it is important that TG data for a polymer represents the thermal decomposition behaviour of the polymer alone, each samples was vacuum dried at 60.0°C to constant weight in order to remove any residual volatiles. The sample, about 3-10 mg in weight, was then heated at a rate of 20.0°C/min under a nitrogen atmosphere. The TG data obtained could be expressed in 2 different ways, i.e., as plot of :

(a) percentage weight of sample remaining (%) against temperature (T)

(b) 1st derivative of weight loss curve, i.e., d(%)/dT

The TG curves are shown in Figures 3.41 - 3.48 and the derived decomposition parameters compared in Table 3.19.

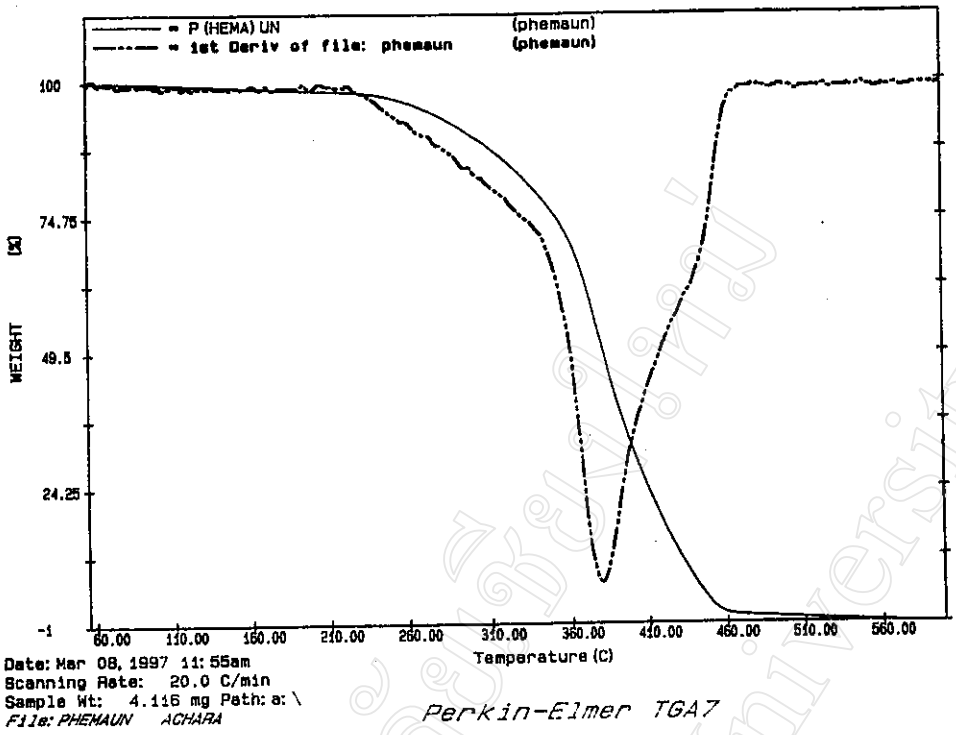


Figure 3.41 : Dynamic TG thermogram and 1st derivative curve of uncrosslinked P(HEMA).

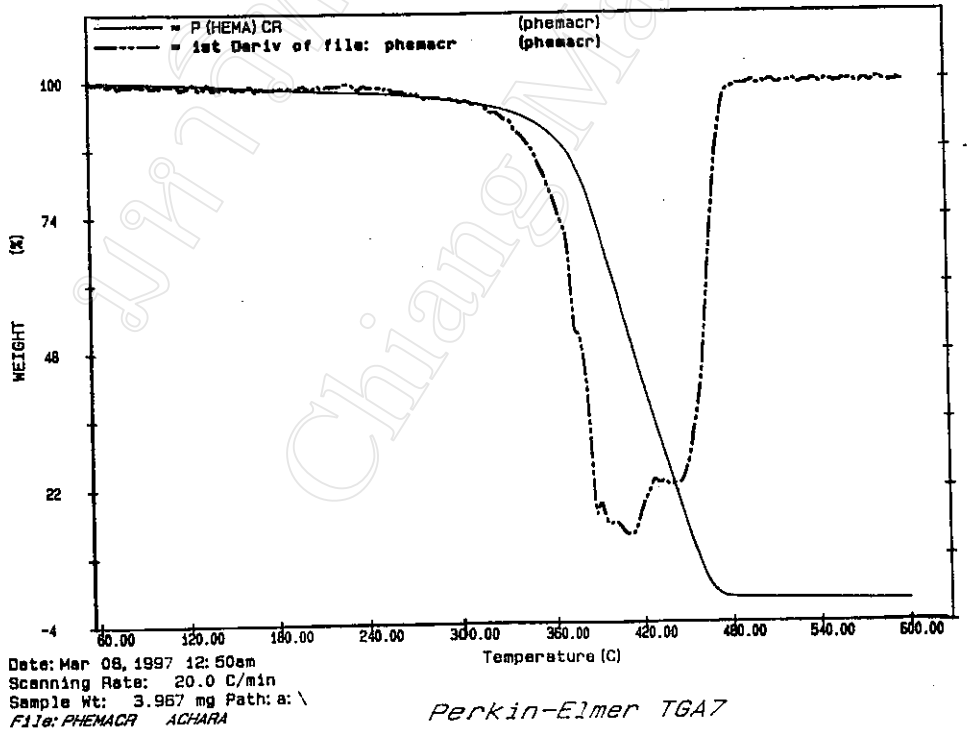


Figure 3.42 : Dynamic TG thermogram and 1st derivative curve of crosslinked P(HEMA).

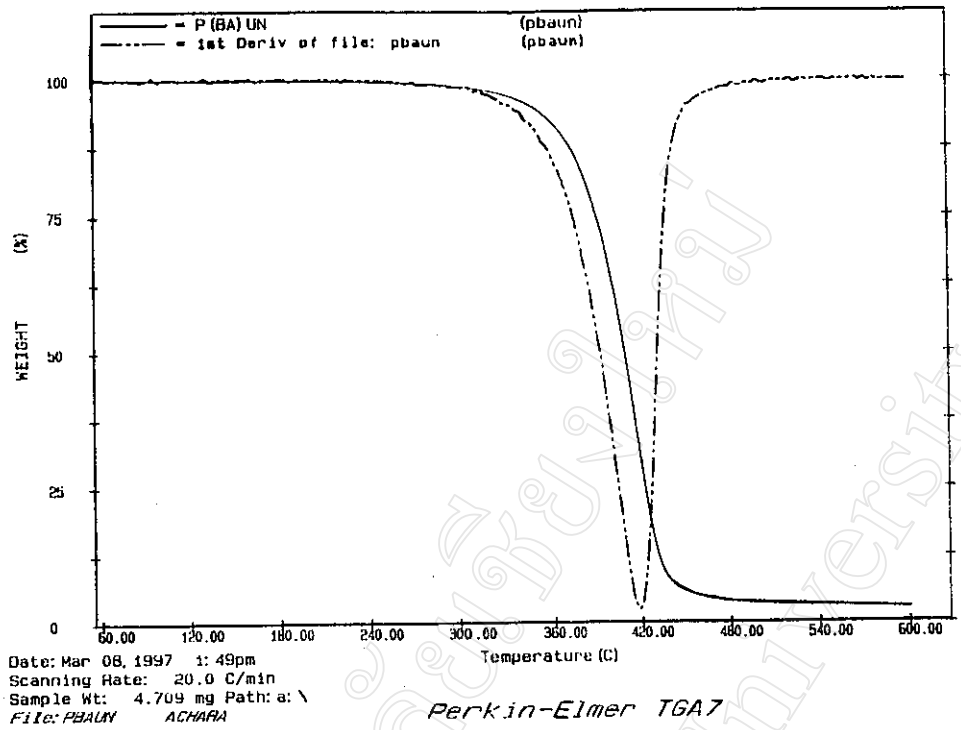


Figure 3.43 : Dynamic TG thermogram and 1st derivative curve of uncrosslinked PBA.

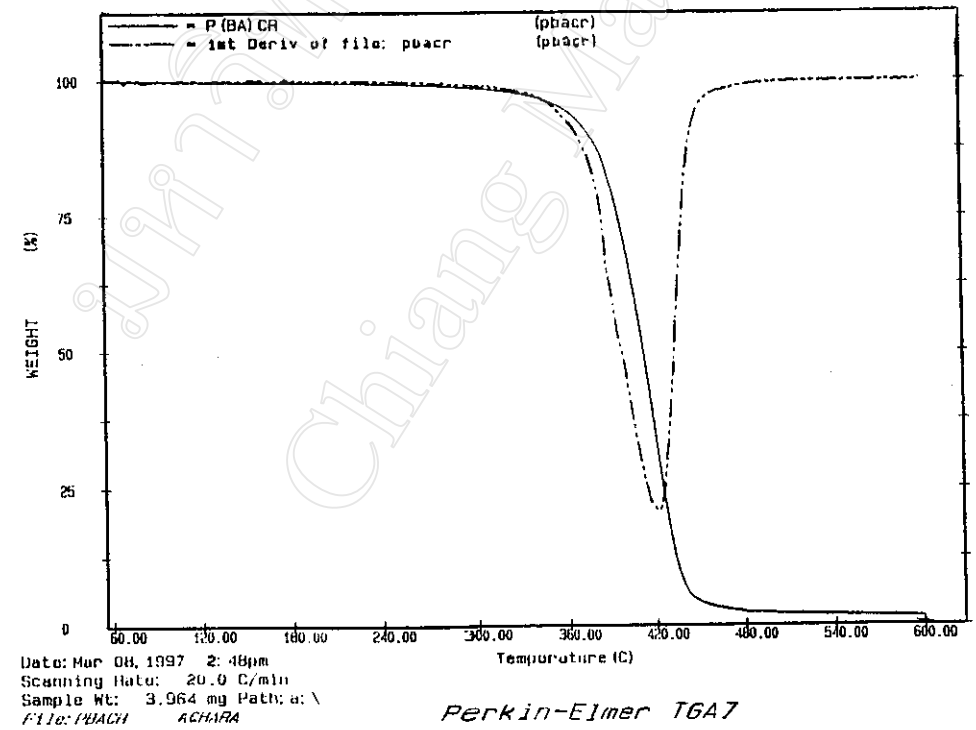


Figure 3.44 : Dynamic TG thermogram and 1st derivative curve of crosslinked PBA.

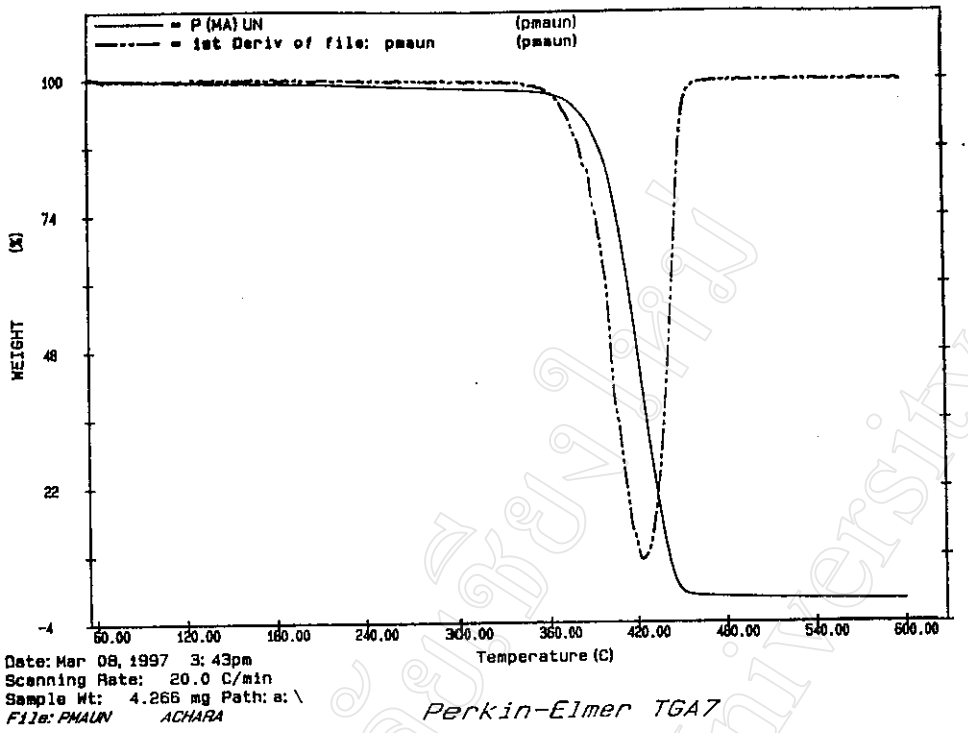


Figure 3.45 : Dynamic TG thermogram and 1st derivative curve of uncrosslinked PMA.

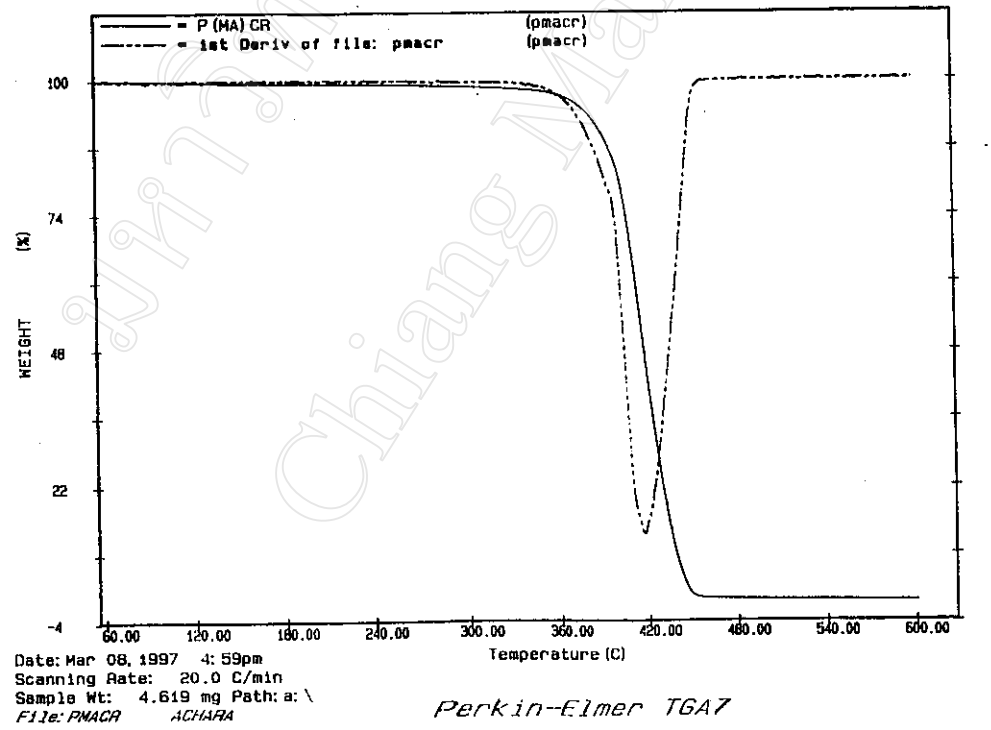


Figure 3.46 : Dynamic TG thermogram and 1st derivative curve of crosslinked PMA.

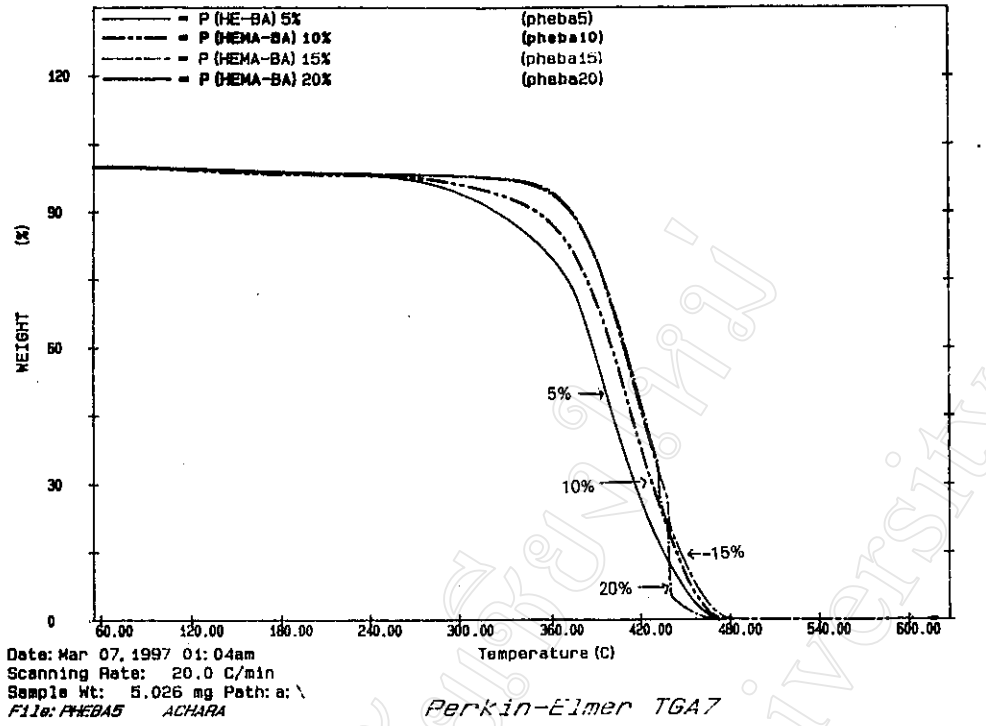


Figure 3.47 : Dynamic TG thermograms of the crosslinked P(HEMA-co-BA) copolymers.

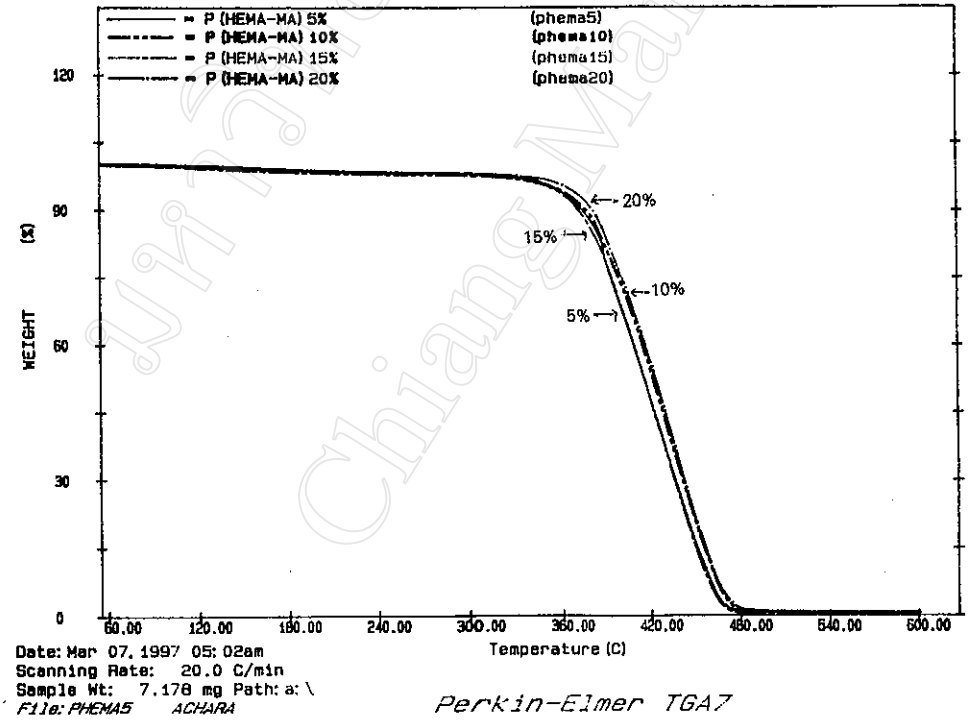


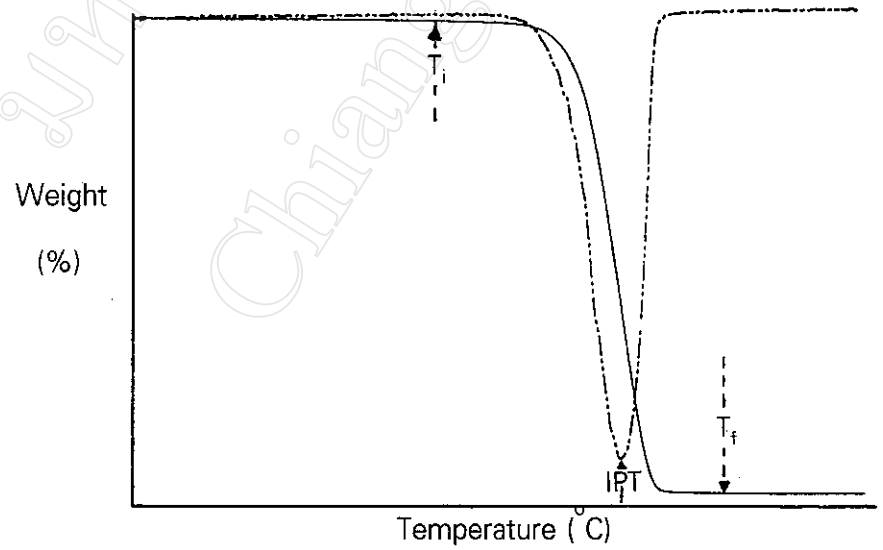
Figure 3.48 : Dynamic TG thermograms of the crosslinked P(HEMA-co-MA) copolymers.

Table 3.19 : Thermal degradation characteristics of the homopolymers and coplymers.

Homopolymer or Copolymer	T_i* (°C)	T_f* (°C)	IPT** (°C)
uncrosslinked P(HEMA)	225	470	380
crosslinked P(HEMA)	300	485	415
uncrosslinked PBA	322	478	420
crosslinked PBA	338	475	420
uncrosslinked PMA	355	458	425
crosslinked PMA	357	460	417
crosslinked P(HEMA-co-BA)/95:5	248	481	-
crosslinked P(HEMA-co-BA)/90:10	260	489	-
crosslinked P(HEMA-co-BA)/85:15	318	490	-
crosslinked P(HEMA-co-BA)/80:20	323	481	-
crosslinked P(HEMA-co-MA)/95:5	315	488	-
crosslinked P(HEMA-co-MA)/90:10	318	489	-
crosslinked P(HEMA-co-MA)/85:15	328	490	-
crosslinked P(HEMA-co-MA)/80:20	335	492	-

* T_i, T_f = initial and final weight loss temperature respectively

** IPT = "Inflection Point Temperature", i.e., temperature at which the maximum rate of weight loss, $(d\%/dT)_{max}$, occurs



3.6 Water Absorption and Retention Properties [40,46]

This part of the work covers the determination of the relative rates of water absorption by thin sheets immersed in water. The water absorbed by a hydrogel network is quantitatively expressed in terms of the "equilibrium water content" and the "water retention" of the polymer.

3.6.1 Water Absorption and Equilibrium Water Content

The equilibrium water content, EWC, is defined mathematically as the ratio of the partial weight of water in the hydrogel to the total weight of the swollen hydrogel *at equilibrium hydration*, expressed as a percentage :

$$EWC = \frac{\text{weight of swollen polymer - weight of dry polymer}}{\text{weight of swollen polymer}} \times 100\% \quad \textit{(at equilibrium)}$$

$$\text{or } EWC = \frac{\text{weight of water in the hydrogel}}{\text{total weight of hydrated hydrogel}} \times 100\% \quad \textit{(at equilibrium)}$$

The EWC is arguably the most important single property of a hydrogel, influencing as it does the water permeability, as well as the mechanical, surface and other properties of the gel. There is a great deal of evidence to suggest that water in polymers can exist in more than one state and that these states of water in a hydrogel will also affect its balance of properties. The water present in a polymer network exists in a continuum of states between two extremes, These are: water strongly associated with the polymer network through hydrogen bonding, sometimes called "bound water", and

water with a much greater degree of mobility, unaffected by the polymeric environment and sometimes referred to as "free water". The properties of a hydrogel are therefore strongly influenced both by its EWC and by the ratio of bound to free water.

In the experimental determination of the EWC, the thickness of the thin moulded sheets obtained from the "*in situ*" bulk polymerisation procedure previously described were measured with a micrometer. Generally, they were found to be within the range of 0.750 ± 0.100 mm. Prior to this, each sample had been vacuum dried at 60°C to constant weight to remove any absorbed moisture. The samples were then immersed in deionized water at 35.0°C in a thermostatically controlled (± 0.1°C) incubator. They were then removed from the water at various time intervals, wiped free of surface moisture with a filter paper (Whatman No.1), weighed immediately, before being re-immersed in the water. In this way the increasing water content (WC) of each sample was followed by measuring the increase in weight with time. The WC was calculated as the average value of three determinations. The increases in water content with immersion time for the homopolymers and copolymers are shown in Tables 3.20 - 3.24 and Figures 3.49 - 3.52.

As the graph in Figures 3.49 - 3.52 show, the water content increases rapidly at first. The rate of water absorption then slows down until, eventually, the water content reaches a constant value at the EWC of the hydrogel. The EWC values of the samples are also indicated in Figures 3.49 - 3.52. In those cases where the terminal approach to the EWC was incrementally slow, rather than continue the experiments to exceedingly long immersion times, the EWC values were estimated to within ± 0.2% by manual extrapolation of the data points.

Table 3.20 : Increasing water contents of the P(HEMA) homopolymers immersed in deionized water for different times at 35.0°C.

Time (min)	Water Content (%, ± 0.01)	
	uncrosslinked P(HEMA)	crosslinked P(HEMA)
0	0.00	0.00
5	12.74	11.27
10	17.73	15.42
15	20.98	18.30
20	23.38	20.70
25	25.12	22.82
30	26.55	24.51
35	27.86	25.99
40	29.27	26.88
45	30.24	27.57
50	31.19	28.22
55	32.17	28.82
60	32.68	29.17
65	33.32	*
70	33.90	30.22
80	34.64	30.50
90	35.23	30.97
100	35.67	31.25
110	35.97	31.50
120	36.24	31.87
150	36.72	32.33
180	36.95	32.68
210	36.24	32.93
300	36.53	33.53
330	36.62	33.64
360	36.90	*
420	37.17	33.64
450	37.22	*

* no data collected

Table 3.21 : Increasing water contents of the PBA homopolymers immersed in deionized water for different times at 35.0°C.

Time (min)	Water content (%, ± 0.01)	
	uncrosslinked PBA	crosslinked PBA
0	0.00	0.00
5	0.63	0.22
10	0.68	0.31
15	0.70	0.35
20	0.72	0.37
25	0.73	0.40
30	0.76	0.42
35	0.77	0.44
40	0.85	0.45
45	0.88	0.46
50	0.92	0.49
55	0.94	0.50
60	0.96	0.51
65	1.00	*
70	1.02	0.51
80	1.05	0.52
90	1.07	0.53
100	1.08	0.54
110	1.17	0.55
120	1.25	0.65
150	1.32	0.68
180	1.35	0.72
225	1.35	0.80
270	*	*
300	1.36	0.84
330	*	0.85
360	*	0.87

* no data collected

Table 3.22 : Increasing water contents of the PMA homopolymers immersed in deionized water for different times at 35.0°C.

Time (min)	Water Content (%, ± 0.01)	
	uncrosslinked PBA	crosslinked PBA
0	0.00	0.00
5	1.10	0.43
10	1.66	0.60
15	1.73	0.70
20	1.92	0.94
25	2.14	1.04
30	2.28	1.06
35	2.38	1.22
40	2.40	1.26
45	2.45	1.26
50	2.50	1.36
55	2.51	1.39
60	2.56	1.39
65	*	1.42
70	2.66	1.46
80	2.75	1.50
90	2.80	1.69
100	2.84	1.69
110	2.87	1.71
120	2.88	1.80
150	2.94	1.86
180	2.97	1.91
210	2.99	*
225	*	2.07
270	3.06	*
285	*	1.03
300	3.15	2.10
360	3.30	*

* no data collected

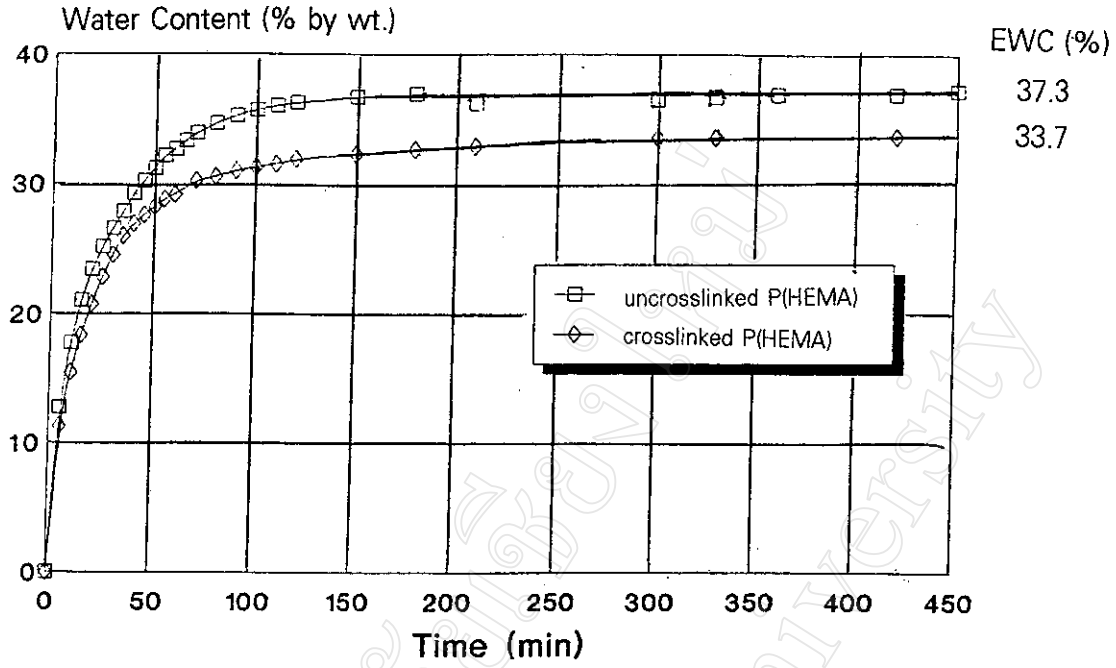


Figure 3.49 : Water content - time profiles for P(HEMA) in deionized water at 35.0°C showing the effect of crosslinking.

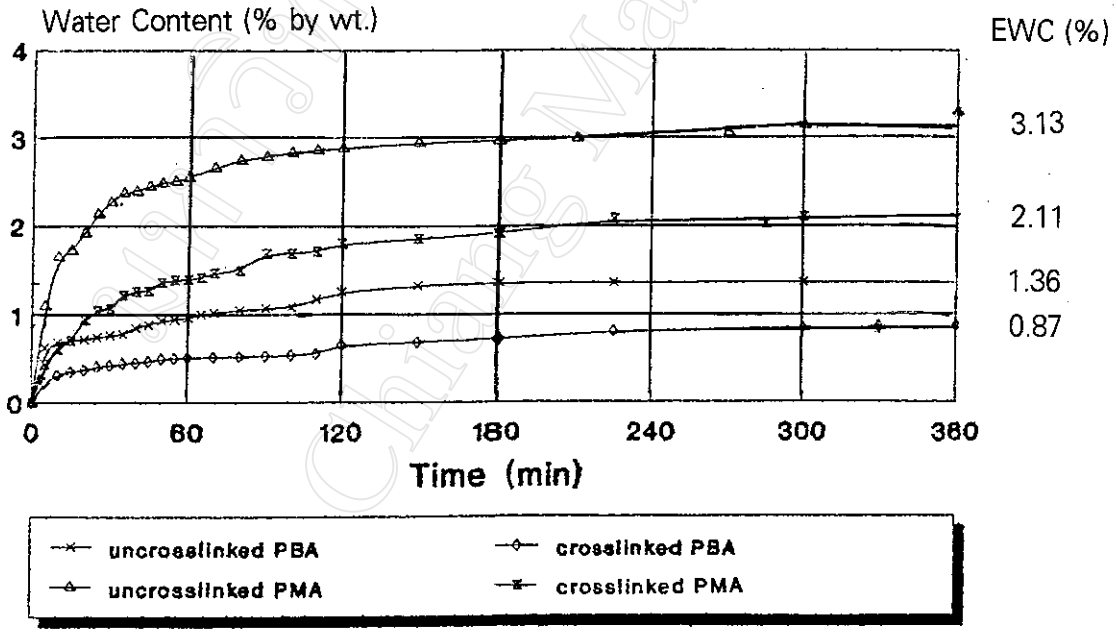


Figure 3.50 : Water content - time profiles for PBA and PMA in deionized water at 35.0°C showing the effects of crosslinking and chemical structure.

Table 3.23 : Increasing water contents of the crosslinked P(HEMA-co-BA) copolymers inmmersed in deionized water for different times at 35.0°C.

Time (min)	Water Content (%, ± 0.01)			
	P(HEMA-co-BA) 95:5	P(HEMA-co-BA) 90:10	P(HEMA-co-BA) 85:15	P(HEMA-co-BA) 80:20
0	0.00	0.00	0.00	0.00
5	7.96	5.66	3.89	2.90
10	11.55	7.99	6.53	4.33
15	13.76	9.62	7.92	5.55
20	15.55	11.02	9.09	6.24
25	16.93	11.90	9.77	6.72
30	18.36	12.17	10.55	7.54
35	20.13	13.79	11.33	8.02
40	21.47	13.91	11.78	8.66
45	22.85	14.55	12.40	9.12
50	24.00	15.23	13.10	9.56
55	25.05	16.00	13.53	9.91
60	25.74	16.70	13.94	10.36
65	26.54	17.20	14.73	10.84
70	27.30	17.83	15.39	11.05
80	27.79	18.94	16.10	11.53
90	28.57	19.80	16.70	12.11
100	28.98	20.65	18.05	12.99
120	29.64	22.32	19.38	13.89
150	29.90	23.68	20.76	15.10
180	29.95	24.72	21.89	16.38
240	30.05	26.15	23.16	18.07
300	30.08	26.74	24.11	19.54
360	30.12	27.27	24.75	20.53
420	30.13	27.27	25.16	21.17
600	30.15	27.40	25.44	22.58

Table 3.24: Increasing water contents of the crosslinked P(HEMA-co-MA) copolymers inmmersed in deionized water for different times at 35.0°C.

Time (min)	Water Content (%, ± 0.01)			
	P(HEMA-co-MA) 95:5	P(HEMA-co-MA) 90:10	P(HEMA-co-MA) 85:15	P(HEMA-co-MA) 80:20
0	0.00	0.00	0.00	0.00
5	12.37	7.99	8.54	7.55
10	17.71	11.38	11.50	10.06
15	21.24	13.51	12.84	11.51
20	25.17	15.26	13.97	13.11
25	28.08	16.71	15.41	14.64
30	29.77	18.27	16.33	15.66
35	30.65	19.60	17.57	16.61
40	31.74	20.91	18.54	17.50
45	32.29	21.88	19.17	18.47
50	32.77	22.82	20.16	19.21
55	33.05	23.67	20.95	19.99
60	33.14	24.45	21.79	21.05
70	33.27	25.76	23.31	22.48
80	33.35	26.90	24.54	23.69
90	33.52	27.76	25.65	24.92
100	33.44	28.63	27.08	25.97
120	33.55	29.91	28.57	27.71
150	33.62	30.91	29.81	28.61
180	33.69	31.65	30.15	29.61
210	33.71	31.92	30.57	30.09
240	33.89	32.23	31.09	30.20
270	*	32.40	31.29	30.32
300	33.81	32.54	31.41	30.35
360	33.90	32.56	31.57	30.38
690	*	32.61	31.71	30.41

* no data collected

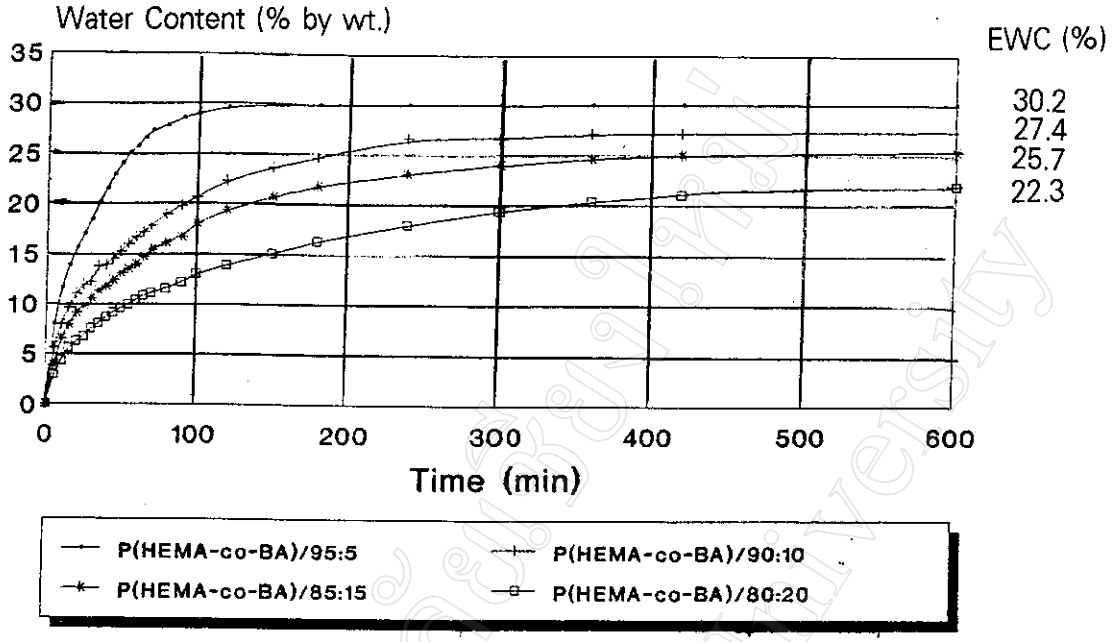


Figure 3.51 : Water content - time profiles for crosslinked P(HEMA-co-BA) in deionized water at 35.0°C showing the effect of copolymer

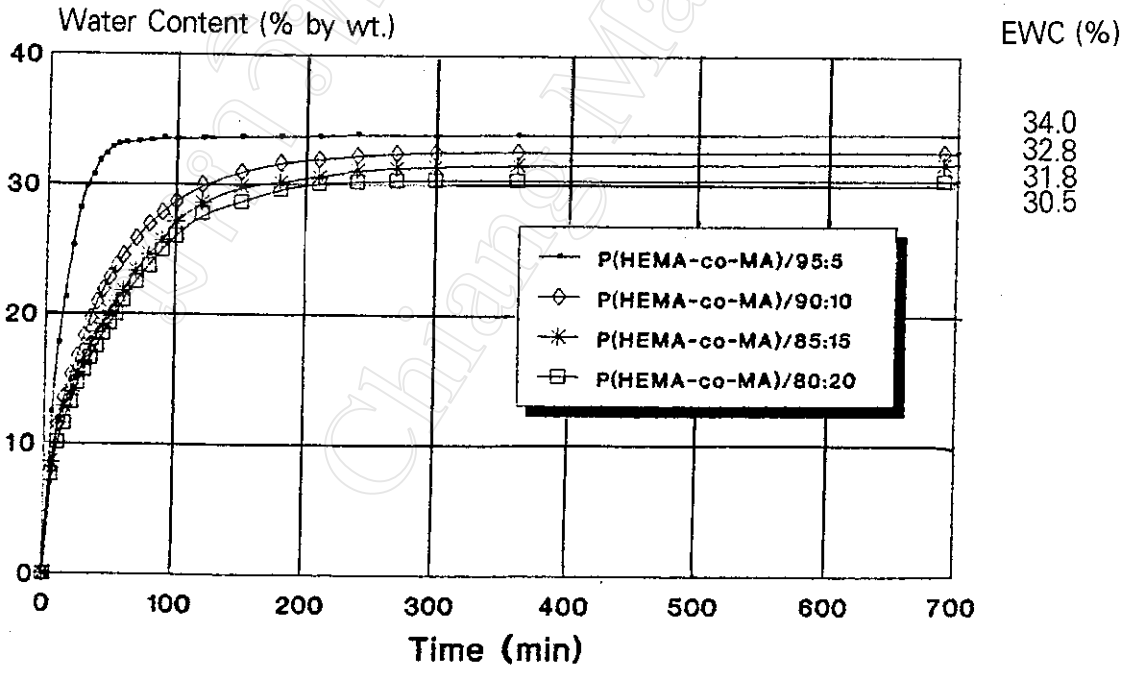


Figure 3.52 : Water content - time profiles for P(HEMA-co-MA) in deionized water at 35.0°C showing the effect of copolymer composition.

The main conclusions that can be drawn from these results are :

(1) Crosslinking decreases both the rate of water absorption and the equilibrium water content of the P(HEMA), PBA and PMA homopolymers.

(2) Copolymerisation of HEMA with a more hydrophobic monomer such as BA or MA decreaes the rate of water absorption and the equilibrium water content. These effects are much more pronounced with BA than MA since the relatively large butyl group in BA is obviously more influential in suppressing hydrogel properties than the small methyl group in MA.

3.6.2 Water Retention

For the study of water retention, test specimens were immersed in deionized water to hydrate to equilibrium for at least 1 day. The hydrated hydrogel specimens were then placed in an incubator at 35.0°C and relative humidity of 55-60%. A temperature of 35.0°C mimics the average temperature of the wound surface [47], while a relative humidity of 55-60% provides an adequate water vapour driving force and resembles that maintained in a typical hospital's Bums Unit [48]. The decreasing water retention of each sample was followed by measuring the decreasing in weight at various time intervals. The water retention was calculated from the equation below as an average of at least three separate determinations. The results obtained are shown in Tables 3.25 - 3.29 and Figures 3.53 - 3.57

$$\text{Water Retention} = \frac{\text{Water Content (at time t)}}{\text{Initial (Equilibrium) Water Content}} \times 100\%$$

Table 3.25 : Water retentions of the P(HEMA) homopolymers as a function of time.

Time (min)	Water Retention (%, ± 0.01)	
	uncrosslinked P(HEMA)*	crosslinked P(HEMA)*
0	100.00	100.00
5	97.39	98.05
10	94.51	95.40
15	91.50	92.81
20	88.80	90.39
25	86.29	88.23
30	83.87	86.62
40	81.21	84.64
50	78.91	82.09
60	76.92	80.00
90	73.41	76.75
120	71.30	74.66
180	68.78	72.46
240	67.50	71.14
300	66.70	70.20
360	66.14	69.64
420	65.73	69.34
480	65.41	69.04
540	65.23	68.79
1380	64.75	67.94
1440	64.64	67.64
1500	64.53	67.59

* Initial (equilibrium) water contents:

uncrosslinked = 37.3 %

crosslinked = 33.7 %

Table 3.26 : Water retentions of the PBA homopolymers as a function of time.

Time (min)	Water Retention (%, ± 0.01)	
	uncrosslinked PBA*	crosslinked PBA*
0	100.00	100.00
5	99.64	99.81
10	99.62	99.77
15	99.60	99.78
20	99.45	99.76
25	99.39	99.74
30	99.36	99.70
40	99.36	99.68
50	99.36	99.64
60	99.35	99.62
90	99.33	99.61
120	99.32	99.60
180	99.31	99.60
240	99.31	99.60
300	99.30	99.60
360	99.30	99.60
420	99.30	99.59
480	99.30	99.59

* Initial (equilibrium) water contents:

uncrosslinked = 1.36 %

crosslinked = 0.87 %

Table 3.27 : Water retentions of the PMA homopolymers as a function of time.

Time (min)	Water Retention (%, ± 0.01)	
	uncrosslinked PMA*	crosslinked PMA*
0	100.00	100.00
5	98.57	99.54
10	98.42	99.37
15	98.27	99.01
20	98.12	98.81
25	98.11	98.71
30	98.01	98.64
40	97.93	98.60
50	97.91	98.54
60	97.87	98.52
90	97.83	98.48
120	97.89	98.48
180	97.81	98.47
240	97.79	98.38
300	97.79	98.38
360	97.78	98.38
420	97.76	98.37
480	97.67	98.37

* Initial (equilibrium) water contents:

uncrosslinked = 3.13 %

crosslinked = 2.11 %

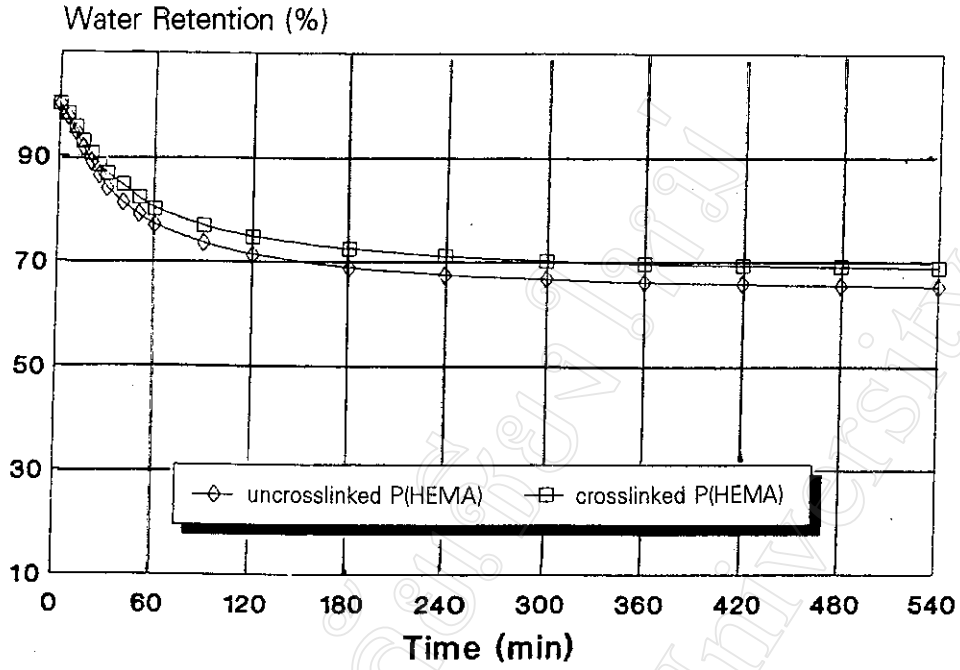


Figure 3.53 : Time dependence of the water retentions of the uncrosslinked and crosslinked P(HEMA) hydrogels in air at 35.0°C.

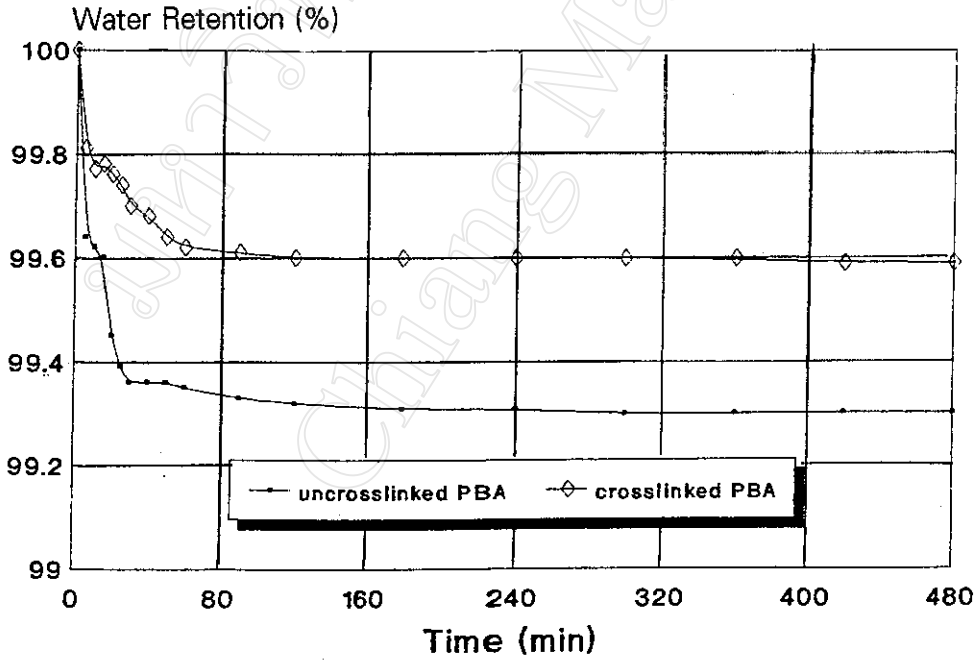


Figure 3.54 : Time dependence of the water retentions of the uncrosslinked and crosslinked PBA hydrogels in air at 35.0°C.

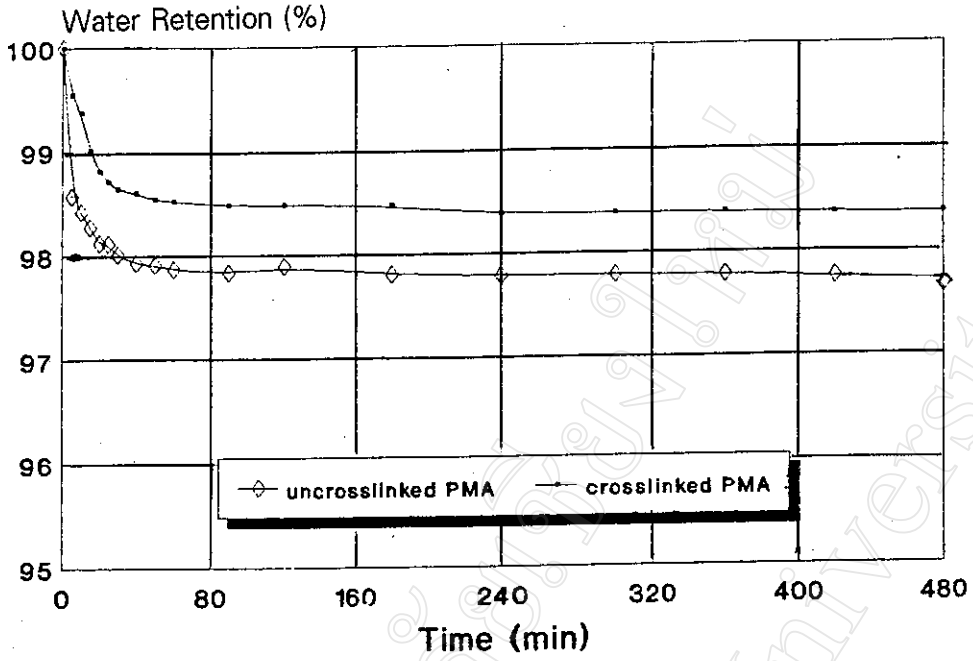


Figure 3.55 : Time dependence of the water retentions of the uncrosslinked and crosslinked PMA hydrogels in air at 35.0°C.

Table 3.28 : Water retentions of the crosslinked P(HEMA-co-BA) copolymers as a function of time.

Time (min)	Water Retention (%, ± 0.01)			
	P(HEMA-co-BA)* 95:5	P(HEMA-co-BA)* 90:10	P(HEMA-co-BA)* 85:15	P(HEMA-co-BA)* 80:20
0	100.00	100.00	100.00	100.00
5	97.23	98.41	98.53	98.64
10	95.27	96.82	96.82	97.54
15	92.70	95.12	95.88	96.51
20	90.47	93.67	94.69	95.35
25	88.87	92.54	93.61	94.81
30	87.31	91.68	93.03	94.00
40	84.57	90.18	91.73	93.43
50	83.03	88.73	90.76	92.57
60	81.19	87.43	89.66	91.38
90	78.73	85.33	87.89	89.82
120	77.10	83.64	85.34	88.86
180	75.25	81.19	83.87	88.99
240	74.21	79.73	81.88	85.18
300	73.74	78.85	80.97	84.42
360	72.99	77.81	80.40	83.40
420	72.57	77.49	79.93	82.64
480	72.23	76.85	79.35	82.15
540	71.92	76.36	78.61	81.53
600	71.25	75.50	77.56	80.61
1380	70.97	74.60	76.99	79.60

* Initial (equilibrium) water contents :

95:5 copolymer = 30.2 %

90:10 copolymer = 27.4 %

85:15 copolymer = 25.7 %

80:20 copolymer = 22.3 %

Table 3.29 : Water retentions of the crosslinked P(HEMA-co-MA) copolymers as a function of time.

Time (min)	Water Retention (%, ± 0.01)			
	P(HEMA-co-MA)* 95:5	P(HEMA-co-MA)* 90:10	P(HEMA-co-MA)* 85:15	P(HEMA-co-MA)* 80:20
0	100.00	100.00	100.00	100.00
5	96.32	97.43	98.13	98.63
10	91.97	95.01	96.47	96.46
15	89.09	91.44	94.48	94.53
20	85.55	89.85	92.62	92.77
25	82.40	87.10	90.77	90.84
30	81.00	84.50	89.36	89.61
40	78.14	81.48	87.71	87.59
50	75.32	80.02	85.44	85.53
60	73.66	78.80	83.51	84.39
90	71.20	75.85	80.53	81.27
120	70.38	73.41	78.76	79.33
180	69.52	71.54	75.70	76.49
240	69.12	71.04	74.95	75.41
300	68.38	70.54	73.60	74.64
360	67.98	70.16	72.77	73.45
420	67.68	69.78	71.89	73.20
480	67.49	69.39	71.22	72.58
540	67.40	68.74	70.33	71.95
1380	67.07	68.24	69.42	70.45

* Initial (equilibrium) water contents :

95:5 copolymer = 34.0 %

90:10 copolymer = 32.8 %

85:15 copolymer = 31.8 %

80:20 copolymer = 30.5 %

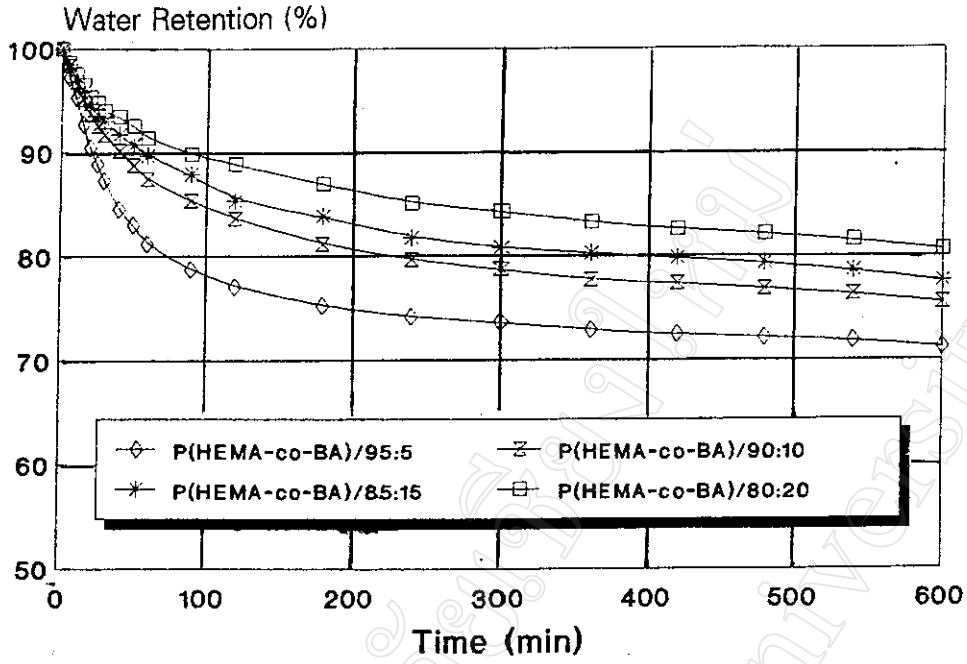


Figure 3.56 : Effect of copolymer composition on the water retention of crosslinked P(HEMA-co-BA) in air at 35.0°C.

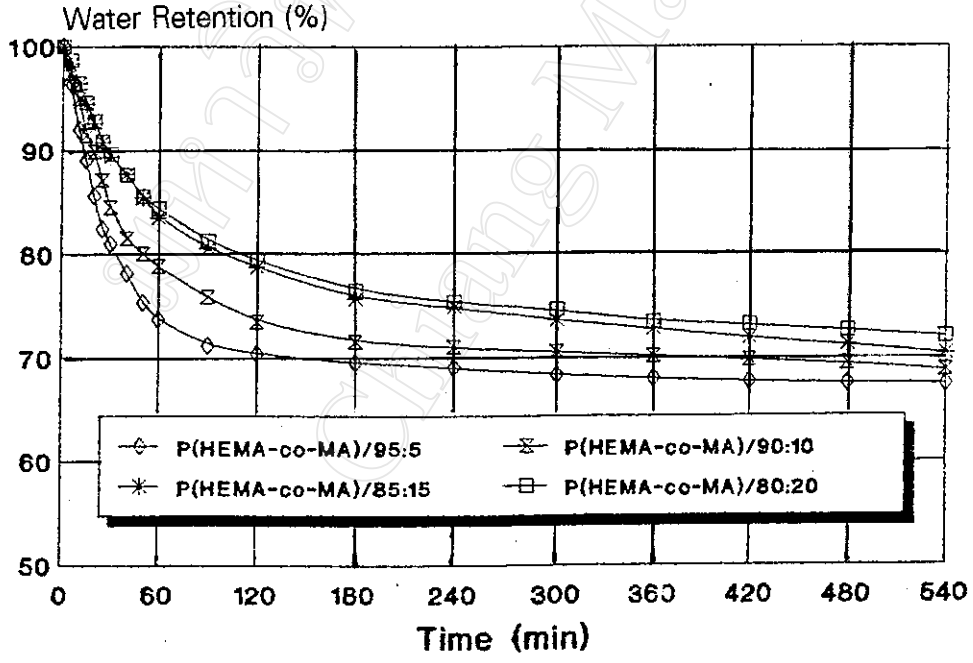


Figure 3.57 : Effect of copolymer composition on the water retention of crosslinked P(HEMA-co-MA) in air at 35.0°C.

As would be expected, the water retention-time profiles in Figures 3.55 - 3.59 are the reverse of the absorption-time profiles, with rapid evaporative water loss at the beginning followed by a slowing down towards a constant (equilibrium) value.

By combining this water retention data with the previous water absorption data, it is possible to calculate (or, at least, estimate) the EWC values of the hydrogels in air as well as in water. These values are compared in Table 3.30 below and are of some relavance to their practical application as wound dressings, as will be discussed in more detail in the following Chapter 4.

Table 3.30 : Comparison of equilibrium water contents (EWC) of the hydrogels studied in both water and air.

Homopolymer or Copolymer	EWC (%, ± 0.2)	
	in WATER *	in AIR **
Uncrosslinked P(HEMA)	37.3	24.1
Crosslinked P(HEMA)	33.7	22.8
Uncrosslinked PBA	1.36	1.35
Crosslinked PBA	0.87	0.87
Uncrosslinked PMA	3.13	3.05
Crosslinked PMA	2.11	2.08
P(HEMA-co-BA) 95:5	30.2	21.4
P(HEMA-co-BA) 90:10	27.4	20.4
P(HEMA-co-BA) 85:15	25.7	19.7
P(HEMA-co-BA) 80:20	22.3	17.8
P(HEMA-co-MA) 95:5	34.0	22.8
P(HEMA-co-MA) 90:10	32.8	22.4
P(HEMA-co-MA) 85:15	31.8	22.1
P(HEMA-co-MA) 80:20	30.5	21.4

* in deionized water at 35.0°C

** in air at 35.0°C, relative humidity 55 - 60%

3.7 Water Vapour Transmission [49,50]

An effective skin substitute should be able to control evaporative water loss from the wound surface. Thermal injury to the skin destroys the semipermeable membrane associated with the lipoprotein layer in the *stratum corneum* [51]. The damage caused allows excessive water to be lost through the injured skin. After thermal injury, the evaporative water loss from the wound surface can be some twenty times greater than normal skin [47]. Insensible water loss can place unacceptable demands on body metabolism, especially in extensive burn injuries. In addition, uncontrolled water loss from the wound surface may cause wound dehydration and induce scar formation, Wenger [52] calculated that 2.43 MJ of energy are lost upon the evaporation of one litre of water; thus, excessive water loss is associated with enormous heat loss. Heat loss can be reduced by maintaining a warm treatment environment, while insensible water loss can be reduced by the application of a temporary skin substitutes. Therefore, one clinical requirement of a successful temporary skin substitute is that it must control the excessive evaporative water loss from the wound surface to provide a moist environment for rapid re-epithelialisation. It should, on one hand, prevent fluid accumulation which might lead to tissue maceration and wound infection and patient discomfort and, on the other hand, should protect the wound from desiccation. The ability to transport water vapour is therefore an important function of the dressing and hence a valuable preclinical assessment is the measurement of the **water vapour transmission rate (WVT)** of the dressing.

The rate of water vapour transmission (WVT) is defined as the weight of water transmitted per unit time and per unit area. An *in vitro* testing procedure recommended by the American Society for the Testing of Materials (ASTM E 96-66) [53] has been commonly used to study the WVT of various skin substitutes. Two

separate techniques, the "Water Cup" method (Procedure B) and the "Inverted Cup" method (Procedure BW) have been employed. In these methods, a disc of the material is mounted on an aluminium cup assembly (Figure 3.58) containing water and placed in a chamber under controlled temperature and humidity. From periodic weighings of the cup, the water loss may be determined and hence the WVT of the material. The cup may be inverted such that the water is in contact with the test material (Inverted Cup procedure) or placed upright (Water Cup procedure) such that an air gap between the water and the material occurs.

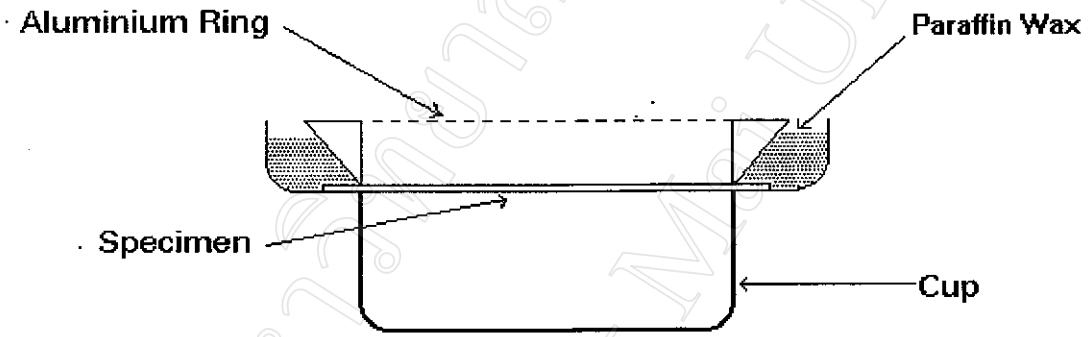


Figure 3.58 : Expanded view of the aluminium cup assembly used for water vapour transmission (WVT) measurements.

The drawback associated with this technique is that a large difference in WVT is observed depending upon the geometry of the cup and the technique employed. This is attributed to the relative humidity gradient developed at the air-membrane interface within the cup. In the "Water Cup" technique, the space between

the membrane and the water within the cup may not reach 100% relative humidity. Such an effect will reduce the WVT of the test membrane. The magnitude of this humidity gradient is dependent upon the water permeability and the nature of the membrane. Whenever it is desired to use the *in vitro* technique, the "Inverted Cup" method should be preferred to the "Water Cup" method as the boundary layer resistance is negligible and the results are less dependent on the geometry of the cup assembly. Therefore, in this research work, only the "Invert Cup" was used .

3.7.1. Inverted Cup Method : Test Procedure

Each test specimen was immersed in deionized water to hydrate to equilibrium for at least 1 day. The hydrated specimen was then cut from the hydrogel sheet using a template with an overall diameter of 7.5 cm. The thickness of each disc specimen was measured at three locations using a micrometer and the mean value calculated. When mounted in the cup, the effective transfer area of the specimen was 28.274 cm^2. Any excess surface water was removed with a filter paper before the hydrated sample was fitted into the water vapour transmission assembly. The test dish was then filled with precisely 20 ml deionized water. This amount of water was such that distorsion of the specimen due to the mass of water was not excessive and the reservoir would not dry out during the test period. After testing for leakage of the assembled cup, the dish assembly was weighed and the cup suspended upside down inside a temperature-controlled incubator at 35.0°C, as shown in Figure 3.59, this being the zero-time (t=0) for the experiment. The internal % relative humidity of the incubator was also recorded. The dish assembly was then re-weighed at various time intervals, each weighing giving a data point at a particular time. Each experiment lasted for a total of 30 hours. At the end of the experiment, it was repeated twice more

using the same sample and the same initial amount of water (20 ml). The results of each run are given in the following tables.

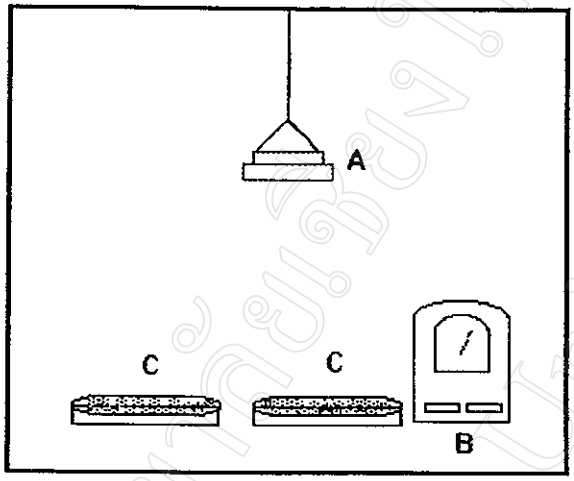


Figure 3.59 : Internal arrangement employed inside the incubator for the "Inverted Cup" method of WVT determination.
A = inverted cup, B = humidity meter, C = silica gel

From the results obtained, the rate of water vapour transmission, WVT, was calculated from the equation below in which the slope of the plot of weight against time (G/t) is divided by the exposed surface area (A) of the specimen. The final value is an average of at least three determinations.

Rate of water vapour transmission [54] :

$$WVT = G/tA = (G/t)/A$$

where G/t = rate of weight loss, g/hr

A = exposed area of specimen (28.274 cm^2), m^2

WVT = rate of water vapour transmission, $g/hr.m^2$

The final WVT value obtained is specific for a given temperature and relative humidity, in these experiments: 35.0°C, 55-60%.

The experimental results are given in the following Tables 3.31-3.44 and an example of a water loss-time graph for the uncrosslinked P(HEMA) hydrogel is shown in Figure 3.60. Only this one graph is shown since all of the samples studied showed similar linear weight losses with time, differing only in their slopes and, hence, WVT values. The results obtained from these graphs of water loss against time, and the calculated values of the WVT, are summarized and compared for all of the samples in Table 3.45.

Table 3.31 : Water vapour transmission test results for uncrosslinked P(HEMA).

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.2932	0.2520	0.2653
2	0.5513	0.4925	0.5039
3	0.8088	0.7356	0.7518
4	1.0811	0.9793	0.9982
5	1.3412	1.2225	1.2463
6	1.6235	1.4702	1.4975
7	1.8818	1.7183	1.7456
8	2.1510	1.9614	*
10	*	*	2.5572
11	2.9936	*	*
12	*	2.9614	*
14	*	*	3.4534
15	3.9821	3.6218	*
18	*	*	4.4616
19	*	4.6081	*
20	5.3215	*	*
21	*	*	5.2329
22	5.9134	5.4221	5.4910
23	6.1538	5.6466	2.7296
24	6.4037	5.8577	5.9737
25	6.6536	*	6.2128
26	6.9102	6.3706	6.4614
27	7.1584	6.5682	6.7054
28	7.4170	6.8382	6.9559
29	7.6702	7.0672	7.2001
30	*	7.2908	*

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

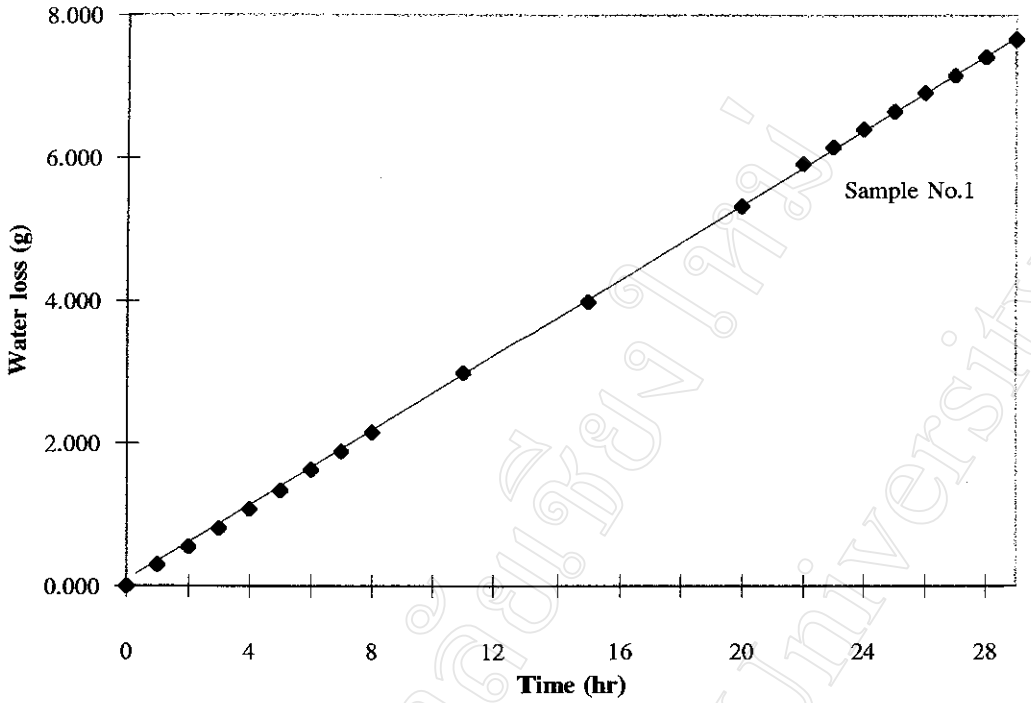


Figure 3.60 : WVT plot for the uncrosslinked P(HEMA) hydrogel.

Sample Calculation :

For Sample No.1 in Table 3.35.

$$\text{Slope} = \frac{6.1538 - 1.6235 \text{ g}}{23 - 6 \text{ hr}}$$

$$= 0.2665 \text{ g/hr}$$

$$\text{WVT} = G/tA = (G/t)/A$$

$$= \frac{0.2665 \text{ g/hr}}{28.274 \times 10^{-4} \text{ m}^2}$$

$$= 94.26 \text{ g/hr.m}^2$$

Table 3.32 : Water vapour transmission test results for crosslinked P(HEMA).

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.2609	0.2378	0.2394
2	0.5409	0.4619	0.4528
3	0.7151	0.6842	0.6768
4	0.9429	0.9086	0.9019
5	1.1830	1.1328	1.1291
6	1.4123	1.3564	1.3610
7	*	1.5791	1.5901
8	*	1.7966	*
9	2.0834	*	*
10	*	*	2.3432
12	2.6895	2.6860	*
14	*	*	3.1095
15	3.3247	3.2512	*
18	4.0085	*	3.9964
19	*	4.1652	*
21	4.7300	*	4.6953
22	4.9471	4.8834	4.9112
23	5.1623	5.0829	5.1110
24	5.3764	5.2761	5.3141
25	5.5989	*	5.5133
26	5.8150	5.7445	5.7177
27	6.0405	5.9246	5.9186
28	6.2610	6.1719	6.1248
29	6.4865	6.3794	6.3240
30	*	6.5925	*

* no data collected

** Inverted Cup method at 35.0 $^{\circ}$C, 55-60% relative humidity

Table 3.33 : Water vapour transmission test results for crosslinked PBA.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.0066	0.0064	0.0062
2	0.0129	0.0122	0.0121
3	0.0203	0.0191	0.0194
4	0.0267	0.0255	0.0245
5	0.0340	0.0323	0.0319
6	0.0410	0.0395	0.0380
7	0.0483	0.0465	0.0452
8	*	*	0.0502
9	*	*	0.0574
10	0.0734	0.0702	0.0690
13	*	*	0.0859
14	0.0952	0.0915	*
15	*	*	0.0967
18	0.1238	0.1158	*
20	*	*	0.1349
21	0.1465	01402	*
22	0.1518	0.1449	*
23	0.1572	0.1508	0.1514
24	0.1607	0.1566	0.1575
25	0.1700	0.1629	0.1633
26	0.1757	0.1687	0.1691
27	0.1830	0.1756	0.1762
28	0.1908	0.1828	0.1811
29	0.1979	0.1900	0.1899
30	*	*	0.1964

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.34 : Water vapour transmission test results for crosslinked PBA.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.0062	0.0067	0.0068
2	0.0124	0.0131	0.0129
3	0.0184	0.0190	0.0190
4	0.0232	0.0250	0.0237
5	0.0300	0.0312	0.0315
6	0.0359	0.0374	0.0362
7	0.0418	0.0431	0.0421
8	0.0480	0.0493	0.0487
9	*	*	0.0554
10	*	*	0.0618
12	0.0742	0.0756	*
13	*	*	0.0799
15	0.0915	0.0939	0.0922
19	0.1167	0.1184	*
20	*	*	0.1235
22	0.1365	0.1372	*
23	0.1426	0.1433	0.1429
24	0.1476	0.1486	0.1480
25	*	*	0.1543
26	0.1605	0.1616	0.1600
27	0.1656	0.1667	0.1663
28	0.1726	0.1732	0.1731
29	0.1794	0.1798	0.1800
30	0.1856	0.1865	0.1862

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.35 : Water vapour transmission test results for uncrosslinked PMA.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.0144	0.0137	0.0142
2	0.0299	0.0261	0.0269
3	0.0436	0.0384	0.0391
4	0.0570	0.0497	0.0501
5	0.0704	0.0621	0.0638
6	0.0845	0.0738	0.0746
7	0.0981	0.0865	0.0869
8	*	0.0975	0.0984
9	*	*	0.1125
10	0.1443	*	0.1214
12	*	0.1484	*
13	*	*	0.1596
14	0.1895	*	*
15	*	0.1825	0.1817
18	0.2412	*	*
19	*	0.2308	*
20	*	*	0.2410
21	0.2861	*	*
22	0.2950	0.2678	*
23	0.3084	0.2807	0.2801
24	0.3210	0.2907	0.2913
25	0.3335	*	0.3018
25	0.3436	0.3170	0.3184
27	0.3592	0.3263	0.3269
28	0.3724	0.3405	0.3408
29	0.3875	0.3529	0.3532
30	*	0.3651	0.3644

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.36 : Water vapour transmission test results for crosslinked PMA.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0. 0104	0.0108	0.0112
2	0.0210	0.0210	0.0215
3	0.0315	0.0316	0.0321
4	0.0424	0.0416	0.0428
5	0.0534	0.0511	0.0514
6	0.0646	0.0603	0.0610
7	0.0761	0.0686	0.0692
8	*	0.0793	0.0798
9	*	*	0.0904
10	0.1153	*	0.1021
12	*	0.1205	*
13	*	*	0.1297
14	0.1475	*	*
15	*	0.1482	0.1502
18	0.1910	*	*
19	*	0.1846	*
20	*	*	0.1938
21	0.2289	*	*
22	0.2371	0.2164	*
23	0.2467	0.2226	0.2242
24	0.2560	0.2336	0.2351
25	0.2663	*	0.2423
25	0.2761	0.2553	0.2564
27	0.2867	0.2624	0.2629
28	0.2967	0.2738	0.2742
29	0.3089	0.2834	0.2846
30	*	0.293	0.2938

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.37 : Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 95:5 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.1668	0.1670	0.1353
2	0.2994	0.2994	0.2740
3	0.4243	0.4242	0.3961
4	0.5536	0.5442	0.5351
5	0.6939	0.6908	0.6807
6	0.8433	0.8725	0.8236
7	1.0017	0.9979	*
8	1.1567	1.1624	*
9	*	1.3315	1.2364
10	1.4509	1.5087	*
12	*	*	1.6532
13	1.9513	1.9742	*
15	*	2.3112	2.0857
18	2.7021	*	2.5016
20	*	3.1048	*
21	*	*	2.9492
22	3.3585	*	3.0896
23	3.5247	3.6337	3.2346
24	3.6816	3.7909	3.3755
25	3.8356	3.9437	3.5224
26	3.9900	4.0888	3.6649
27	4.1427	4.2413	3.8121
28	4.2997	4.3978	3.9608
29	4.4546	4.5527	4.1124
30	4.6093	4.7072	*

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.38 : Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 90:10 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.1345	0.1379	0.1367
2	0.2139	0.2653	0.2417
3	0.3087	0.3649	0.3326
4	0.4114	0.4737	0.4170
5	0.5008	0.5825	0.4983
6	0.5798	0.6859	0.5781
7	0.6847	*	0.6555
8	0.7576	*	0.7307
9	0.8586	0.9706	*
10	0.9512	*	0.8259
12	*	1.1545	*
13	1.2138	*	1.1033
15	1.4216	1.4508	*
18	*	1.7129	1.4165
20	1.8659	*	*
21	*	2.0202	*
22	*	2.0971	1.7257
23	2.1275	2.1721	1.7965
24	2.2014	2.2445	1.8610
25	2.3005	2.3169	1.9248
26	2.3624	2.3871	1.9879
27	2.4570	2.4568	2.0496
28	2.5638	2.5282	2.1133
29	2.6411	2.6012	2.1749
30	2.7405	*	2.2361

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.39 : Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 85:15 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.1217	0.0960	0.1713
2	0.2360	0.1815	0.2586
3	0.3252	0.2674	0.3324
4	0.4213	0.3341	0.4231
5	0.5160	0.4031	0.5178
6	0.6055	0.4651	0.5894
7	*	*	0.6423
8	*	*	0.7144
9	0.8409	0.6198	0.8041
10	*	*	0.8756
12	1.0187	0.9427	*
15	1.2532	1.1649	1.2630
18	1.5065	1.4011	*
20	*	*	1.6436
21	1.7505	1.6028	*
22	1.8238	1.6986	*
23	1.8973	1.7356	1.8886
24	1.9687	1.9069	1.9578
25	2.0430	1.9670	2.0510
26	2.1153	2.0427	2.1231
27	2.1910	2.1043	2.2125
28	2.2674	2.1611	2.2749
29	2.3422	2.2178	2.3528
30	*	*	2.4229

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.40 : Water vapour transmission test results for crosslinked P(HEMA-co-BA) / 80:20 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.1111	0.0947	0.1145
2	0.1884	0.1604	0.1619
3	0.2573	0.2170	0.2234
4	0.3276	0.2687	0.2692
5	0.3964	0.3188	0.3098
6	0.4612	0.3677	0.3667
7	0.5231	0.4160	0.4034
8	0.5828	0.4642	0.4658
9	*	*	0.5019
10	0.6893	0.5219	0.5346
13	0.8824	0.7015	0.6594
15	*	*	0.7628
18	1.1312	0.8812	*
20	*	*	0.9817
22	1.3845	1.0840	*
23	1.4415	1.1282	1.1264
24	1.4964	1.1696	1.1766
25	1.5487	1.2119	1.2232
26	1.6011	1.2542	1.2548
27	1.6525	1.2955	1.3071
28	1.7069	1.3391	1.3401
29	1.7586	1.3814	1.4018
30	1.8105	1.4249	1.4564

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.41 : Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 95:5 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.2312	0.2454	0.2245
2	0.4495	0.4624	0.4299
3	0.6676	0.8682	0.6366
4	0.8913	0.9125	0.8461
5	1.1168	1.1368	1.0572
6	1.3427	1.3668	1.2733
7	1.5711	1.5896	1.4911
8	1.7900	*	1.7058
10	2.2235	2.3207	*
12	*	*	2.5967
13	2.9328	*	*
14	*	3.1156	*
15	*	*	3.2148
18	3.9624	4.0098	*
19	*	*	4.0569
21	*	4.7037	*
22	4.8970	4.9335	4.8023
23	5.1276	5.1478	5.0011
24	5.3465	5.3675	5.1866
25	5.5611	5.5811	*
26	5.7793	5.8041	5.6367
27	5.9988	6.0238	5.8079
28	6.2199	6.2504	6.0425
29	6.4423	6.4688	6.2386
30	6.6657	*	6.4310

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.42 : Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 90:10 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.1955	0.2437	0.2548
2	0.3722	0.4484	0.4661
3	0.5485	0.6221	0.6125
4	0.7210	0.8123	0.8204
5	0.9001	1.0076	1.0059
6	1.0758	1.1922	1.1776
7	1.2533	*	1.3142
8	1.4336	*	1.5074
9	*	1.7313	1.6912
10	1.8115	*	1.8637
12	*	2.0089	*
13	2.3573	*	2.5064
15	*	2.7345	2.7259
18	3.3218	3.2501	*
19	*	*	3.6145
21	*	3.8047	*
22	4.0427	3.9741	*
23	4.2471	4.1427	4.1709
24	4.4415	4.3097	4.3085
25	4.6335	4.4813	4.4794
26	4.8270	4.6487	4.6528
27	5.0186	4.8231	4.8311
28	5.2147	4.9945	5.0129
29	5.4085	5.1671	5.2014
30	5.5991	*	5.3508

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.43 : Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 85:15 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.1764	0.1750	0.2315
2	0.3137	0.3091	0.3548
3	0.4498	0.4314	0.4523
4	0.5811	0.5494	0.5964
5	0.7116	0.6703	0.7102
6	0.8440	0.7898	0.8589
7	0.9716	0.9100	0.9654
8	*	1.0283	1.0511
9	*	*	1.1842
10	1.3899	1.2091	1.3156
13	*	1.6128	1.6762
14	1.7928	*	*
15	*	*	1.9222
18	2.2711	2.1110	*
20	*	*	2.5089
21	2.6938	*	*
22	2.8090	2.6047	*
23	2.9193	2.7178	2.9142
24	3.0319	2.8233	3.0428
25	3.1398	2.9281	3.1475
26	3.2512	3.0318	3.2749
27	3.3602	3.1345	3.3512
28	3.4731	3.2394	3.4861
29	3.5809	3.3422	3.5548
30	*	3.4447	3.6874

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.44 : Water vapour transmission test results for crosslinked P(HEMA-co-MA) / 80:20 copolymer.

Time (hr)	Water Loss (g) **		
	No.1	No.2	No.3
0	0	0	0
1	0.2221	0.1902	0.2519
2	0.3795	0.3370	0.3626
3	0.4964	0.4683	0.4787
4	0.6189	0.5932	0.5849
5	0.7432	0.7144	0.6711
6	0.8571	0.8318	0.7820
7	*	0.9470	0.8871
8	*	1.0574	1.0236
9	1.1823	*	1.1242
10	*	1.1989	1.2072
12	1.4437	*	*
13	*	1.5986	1.5184
15	1.7504	*	1.7502
18	2.0587	2.0342	*
20	*	*	2.2589
21	2.4325	*	*
22	2.5326	2.5137	*
23	2.6317	2.6192	2.6276
24	2.7278	2.7174	2.7334
25	2.8262	2.8142	2.8458
26	2.9229	2.9110	2.9227
27	3.0221	3.0063	3.0364
28	3.1187	3.1030	3.1189
29	3.2156	3.1994	3.2078
30	*	3.2967	3.3265

* no data collected

** Inverted Cup method at 35.0°C, 55-60% relative humidity

Table 3.45 : Comparison of the WVT rates for all of the homopolymers and copolymers studied in this work : "Inverted cup" method.

Sample	WVT ($g/hr.m^2$)			
	1	2	3	average
uncrosslinked P(HEMA)	94.26	86.12	88.10	87.1*
crosslinked P(HEMA)	78.02	77.24	77.28	77.5
uncrosslinked PBA	2.39	2.30	2.35	2.4
crosslinked PBA	2.20	2.20	2.17	2.2
uncrosslinked PMA	4.63	4.28	4.31	4.4
crosslinked PMA	3.75	3.40	3.37	3.5
crosslinked P(HEMA-co-BA) 95:5	55.46	56.98	50.08	56.2*
crosslinked P(HEMA-co-BA) 90:10	31.37	30.66	25.61	31.0*
crosslinked P(HEMA-co-BA) 85:15	27.30	27.62	27.13	27.4
crosslinked P(HEMA-co-BA) 80:20	20.16	16.30	16.06	16.2*
crosslinked P(HEMA-co-MA) 95:5	78.30	78.73	76.96	78.0
crosslinked P(HEMA-co-MA) 90:10	66.03	61.43	61.43	61.4*
crosslinked P(HEMA-co-MA) 85:15	42.72	39.90	42.44	42.6*
crosslinked P(HEMA-co-MA) 80:20	37.45	36.54	37.45	37.2

* average WVT of the 2 values which are in close agreement (where the 3rd value is significantly different)

As would be expected, the WVT rates in Table 3.45 show similar trends to the EWC values previously. If the EWC is relatively high, then the WVT rate will be relatively high too since the one is dependent on the other.

Even though each and every WVT determination gave a good straight line graph of weight loss against time, there were still significant variations between the three WVT values obtained for each sample. Possible causes of these variations may have been:

(1) Development or closure of microscopic leak points (e.g., pin holes) in or around the sample

(2) Paraffin wax (sealant) contamination around the edges of the sample

(3) Temperature and/or % relative humidity variations inside the incubator

3.8 Mechanical Properties [47]

An effective temporary skin substitute should have adequate toughness to withstand handling and be elastic and flexible to allow conformation to uneven body surfaces. Skin substitutes with exceptional mechanical properties, i.e. high tensile strength, excellent elasticity and flexibility, are required for covering hand burns, facial burns and burns incurred around the joints. The membranes should not restrict the mobility of the injured areas as limited movements will retard recovery of the wound area and promote hypertrophic scarring and contracture. The mechanical properties of a temporary skin substitute are usually described by its tensile strength at break, elongation at break and Young's modulus [55]. The tensile strength at break measures the toughness of the skin substitute. It is the maximum tensile stress sustained by the specimen during the test and its calculated by dividing the maximum load by the original minimum cross-sectional area of the specimen. The maximum stress at the moment of rupture is designated as the tensile strength at break. The elongation at

break is related to the elasticity of the membrane and is calculated by dividing the elongation at the moment of rupture by the initial length multiplied by 100. The Young's modulus is a measure of the stiffness of the membrane and is calculated from the initial slope of the stress-strain curve.

3.8.1 Definitions of Terms Relating to Tensile Testing [56-58]

1. Mechanical Properties : those properties of a material that are associated with elastic and inelastic reactions when an external force is applied, or that involve the relationship between stress and strain.

2. Strain : the ratio of the elongation to the guage length of the test specimen, that is, the change in length per unit original length. It is usually expressed as a dimensionless ratio or as a percentage.

3. Stress : the intensity at a point in a body of the internal forces or components of force that act on a given plane through the point. Stress is expressed in units of force per unit of area.

4. Stress-Strain Diagram or Curve : a diagram in which corresponding values of stress and strain are plotted against each other.

5. Tensile Stress : the tensile load per unit area of minimum original cross-section, within the guage boundaries, carried by the test specimen at any given moment. It is expressed in units of force per unit area.

6. Tensile Strength : the maximum tensile stress sustained by the specimen during a tension test. When the maximum stress occurs at the yield point, it is designated as tensile strength at yield. When the maximum stress occurs at break, it is designated as tensile strength at break.

7. Guage Length : the original length of that portion of the specimen over which the strain or change in length is determined.

8. Elongation : the increase in length produced in the guage length of the test specimen by a tensile load. It is expressed in units of length and is also referred to as extension or displacement.

9. Percentage Elongation at Yield : the percentage elongation at the moment the yield point is attained in the test specimen.

10. Percentage Elongation at Break : the percentage elongation at the moment of rupture of the test specimen.

11. Yield Point : the first point on the stress-strain curve at which an increase in strain occurs without an accompanying increase in stress (Figure 3.63).

12. Yield Strength : the stress at which a material exhibits a specified limiting deviation from the proportionality of stress to strain. It is calculated by dividing the load at the yield point by the original minimum cross-sectional area of the specimen and is expressed in units of force per unit area.

13. Modulus of Elasticity : the ratio of stress to corresponding strain below the proportional limit of a material. It is expressed in terms of force per unit area and is also known as the Elastic Modulus or Young's Modulus.

A typical tensile stress-strain curve for thermoplastic materials is given in Figure 3.61 [41]. The initial part of the stress-strain curve is approximately linear. The stress at the first knee in the curve is usually called the **yield point**. The ratio of stress to strain in the linear portion of the curve is the **modulus of elasticity** in tension and indicates the stiffness of the material.

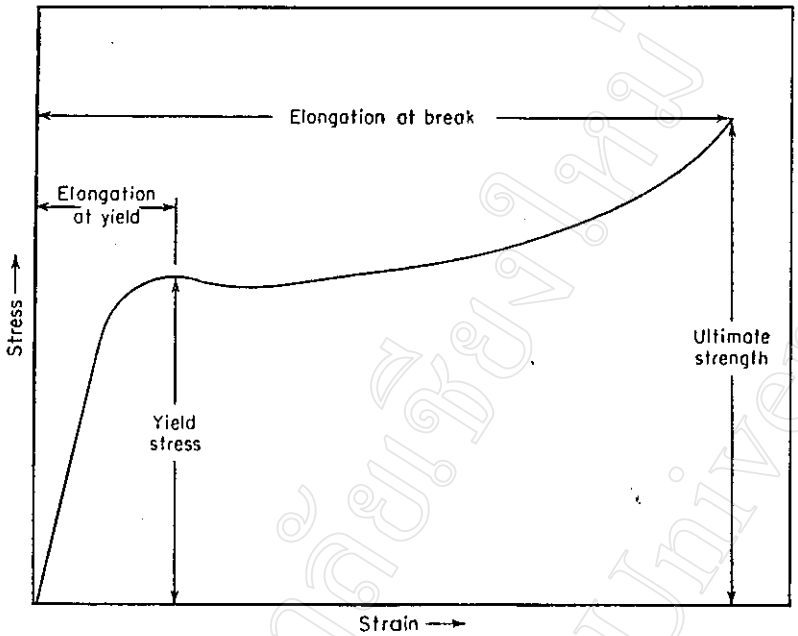


Figure 3.61 : Typical stress-strain curve for thermoplastic materials [41].

However, there are many variations in the shape of the stress-strain curve shown in Figure 3.61, depending upon the nature of the material. Some of the more common variations are compared in Figure 3.62 and are generally classified as follows:

Soft, weak materials have a low modulus, low yield point, and moderate elongation at break.

Hard, brittle materials possess a high modulus, no well-defined yield point, and low elongation at break.

Soft, tough materials show a low modulus, low yield point, and a high elongation at break, with the point of rupture usually considerably higher than the yield point.

Hard, strong materials have a high modulus, high yield point, a moderate elongation at break, and a high breaking stress.

Hard, tough materials show a high modulus. high yield point, high elongation, and a high breaking stress.

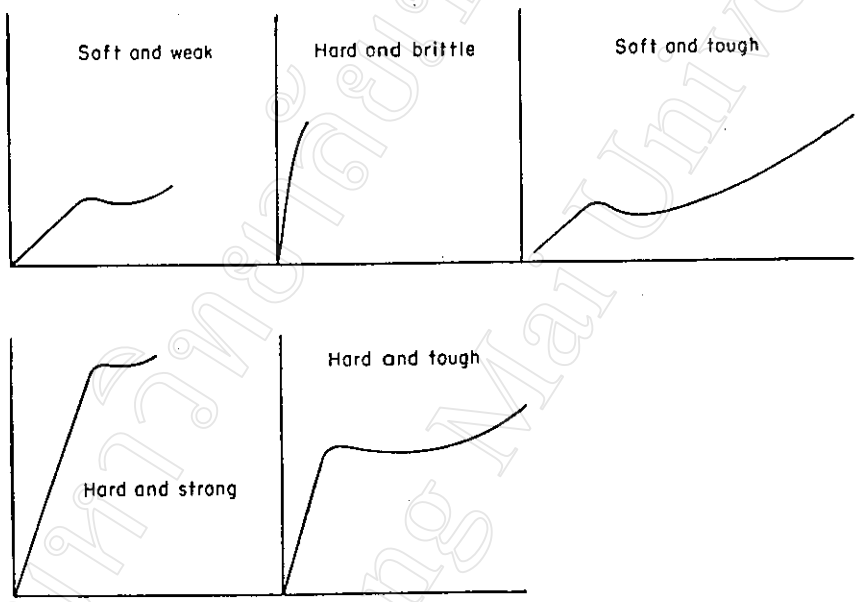


Figure 3.62 : Different types of stress-strain curves [41].

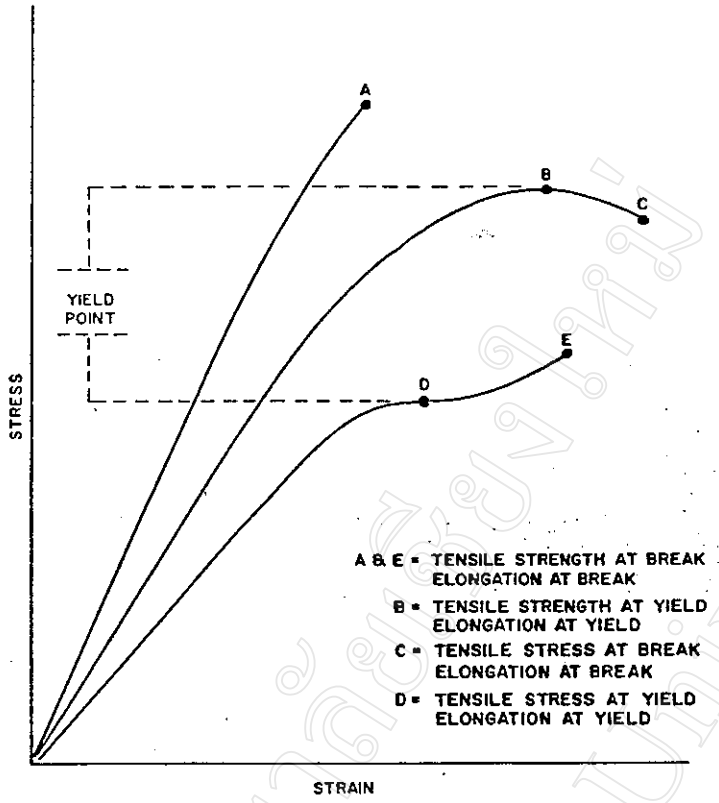


Figure 3.63 : Tensile stress-strain curve designations [56].

3.8.2. Tensile Test Procedure

In this research work, the mechanical properties of the hydrogel samples were determined using an Instron Series 5500 Materials Testing System employing a 10 N load cell and interfaced with a computer. Each specimen was immersed in deionized water at room temperature to hydrate for at least 1 day before being cut into a dumb-bell shape with a Tensile Specimen Press. The thickness of each specimen was determined by a micrometer at three different points along the guage length. Any surface water was removed with filter paper before the hydrated specimen was clamped between the jaws of the testing machine. The specimens were tested under the following conditions:

Guage length	:	40 mm
Guage width length	:	6 mm
Sample thickness	:	0.900 ± 0.150 mm
Load cell	:	10 N
Cross-head speed	:	10 mm/min
Temperature	:	23.0 ± 1.0°C
% Humidity	:	50%

The tensile strength, elongation at break and Young's modulus of the sample under test were calculated. In additon, the instrument's software program enabled stress-strain and load-elongation curves to be plotted and performed a statistical analysis of the three tests run on each sample.

Examples of the stress-strain curves for the uncrosslinked P(HEMA) and crosslinked PMA hydrogels are shown in Figures 3.64-3.65. The calculated values of the various mechanical property terms are given in Tables 3.46-3.59 and then collectively compared in Table 3.60. The units given in these tables are defined as follows:

mm	=	millimetres	=	10^{-3} m
N	=	newtons	=	$kg.m.s^{-2}$
Pa	=	pascals	=	$N.m^{-2}$ = $kg.m^{-1}.s^{-2}$

These units of mm, N, and Pa are therefore units of length, force, and pressure respectively.

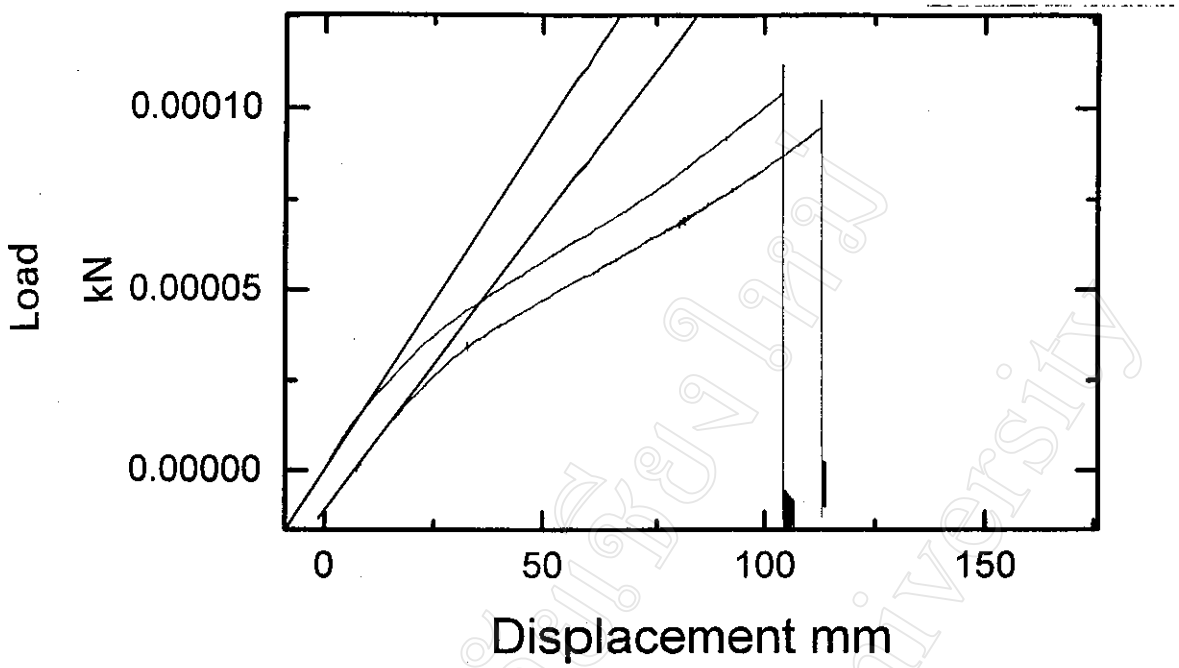


Figure 3.64 : Stress-strain curves of the uncrosslinked P(HEMA) homopolymer, plotted as load against displacement (elongation).

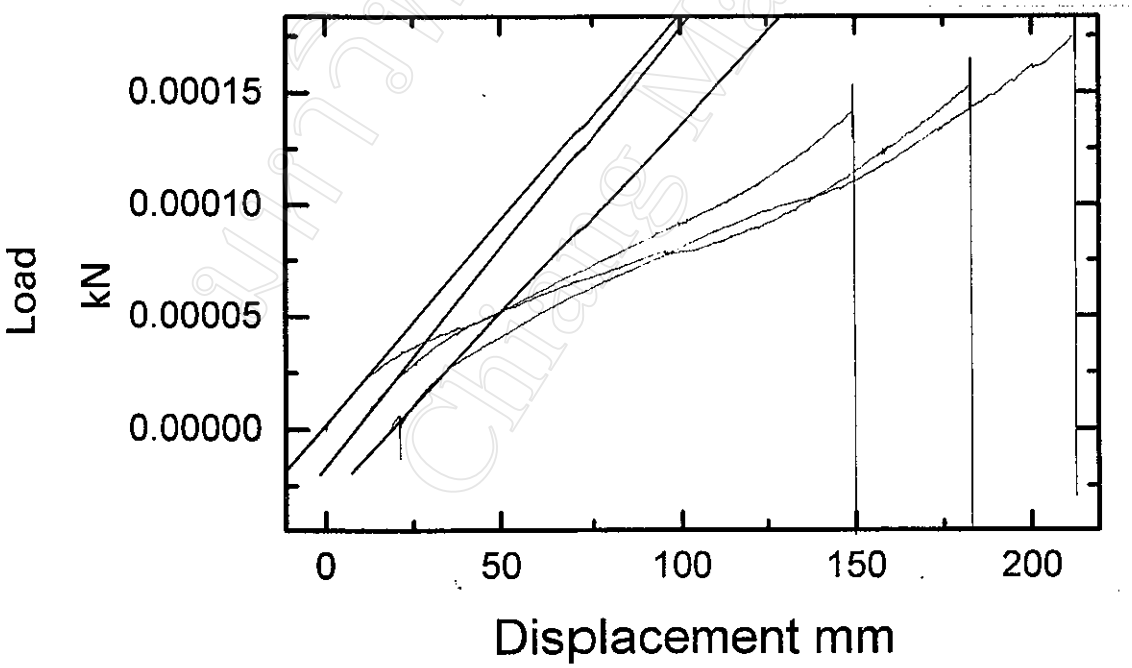


Figure 3.65 : Stress-strain curves of the crosslinked PMA homopolymer, plotted as load against displacement (elongation).

Table 3.46 : Mechanical property test results for the hydrated uncrosslinked P(HEMA) homopolymer (EWC ≈ 37.3%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	133	0.137	24.3	333	14.8
2	104	0.105	18.5	260	13.2
3	106	0.095	16.7	264	11.5
Mean	114	0.112	19.9	286	13.2

Table 3.47 : Mechanical property test results for the hydrated crosslinked P(HEMA) homopolymer (EWC ≈ 33.7%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	32	0.065	11.5	80	30.9
2	41	0.118	21.3	102	32.8
3	38	0.113	20.5	95	34.2
Mean	37	0.099	17.8	92	32.6

Table 3.48 : Mechanical property test results for the uncrosslinked PBA homopolymer (EWC = 1.36%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	248	0.059	10.3	621	7.3
2	210	0.047	8.3	526	6.6
3	258	0.057	9.9	645	5.0
Mean	239	0.054	9.5	597	6.3

Table 3.49 : Mechanical property test results for the crosslinked PBA homopolymer (EWC = 0.87%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	63	0.045	8.8	158	12.5
2	56	0.042	8.1	140	10.6
3	54	0.038	7.4	134	14.1
Mean	58	0.042	8.1	144	12.4

Table 3.50 : Mechanical property test results for the uncrosslinked PMA homopolymer (EWC = 3.13%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	562	0.338	72.3	1,405	9.5
2	579	0.331	70.7	1,449	14.4
3	582	0.360	76.9	1,455	12.1
Mean	574	0.343	73.3	1,436	12.0

Table 3.51 : Mechanical property test results for the crosslinked PMA homopolymer (EWC = 2.11%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	183	0.153	32.7	457	15.7
2	140	0.141	30.2	350	16.7
3	194	0.178	38.0	486	14.2
Mean	172	0.157	33.6	431	15.5

Table 3.52 : Mechanical property test results for the hydrated crosslinked P(HEMA-co-BA) 95:5 copolymer (EWC = 30.2%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	59	0.149	23.4	148	27.1
2	64	0.111	17.5	160	35.0
3	68	0.208	23.6	170	26.4
Mean	63	0.156	21.5	159	29.5

Table 3.53 : Mechanical property test results for the crosslinked P(HEMA-co-BA) /90:10 copolymer (EWC = 27.4%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	80	0.219	35.1	199	26.6
2	85	0.228	36.6	212	26.7
3	89	0.278	44.5	222	27.2
Mean	85	0.242	38.7	211	26.8

Table 3.54 : Mechanical property test results for the crosslinked P(HEMA-co-BA) /85:15 copolymer (EWC = 25.7%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	82	0.149	26.5	205	45.3
2	99	0.208	36.8	248	19.3
3	90	0.207	35.2	225	21.9
Mean	90	0.188	32.8	226	28.8

Table 3.55 : Mechanical property test results for the crosslinked P(HEMA-co-BA) /80:20 copolymer (EWC = 22.3%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	110	0.202	35.4	274	16.5
2	123	0.259	45.4	308	22.0
3	121	0.259	45.4	302	22.4
Mean	118	0.240	42.1	295	20.3

Table 3.56 : Mechanical property test results for the crosslinked P(HEMA-co-MA) /95:5 copolymer (EWC = 34.0%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	68	0.081	13.7	171	28.8
2	61	0.161	27.0	153	26.6
3	60	0.129	21.7	151	21.4
Mean	63	0.124	20.8	158	25.6

Table 3.57 : Mechanical property test results for the crosslinked P(HEMA-co-MA) /90:10 copolymer (EWC = 32.8%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	66	0.116	20.1	165	21.7
2	83	0.192	33.3	208	21.2
3	88	0.218	37.9	220	22.9
Mean	79	0.175	30.4	197	21.9

Table 3.58 : Mechanical property test results for the crosslinked P(HEMA-co-MA) /85:15 copolymer (EWC = 31.8%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	61	0.183	30.8	153	29.7
2	75	0.238	40.1	189	27.5
3	66	0.091	30.2	165	23.0
Mean	67	0.171	33.7	169	26.7

Table 3.59 : Mechanical property test results for the crosslinked P(HEMA-co-MA) /80:20 copolymer (EWC = 30.5%).

Sample No.	Displacement at Max. Load (mm)	Load at Max. Load (N)	Tensile Strength (kPa)	% Elongation at Break (%)	Young's Modulus (kPa)
1	84	0.238	39.6	211	22.1
2	81	0.278	46.3	203	33.0
3	73	0.258	42.2	183	29.6
Mean	79	0.258	42.7	199	28.2

The mechanical property values for the samples studied, as given in Tables 3.46-3.59, are brought together for ease of comparison in Table 3.60 below. These values determine how strong, flexible and extensible each material will be, properties which would be important to its application as a temporary skin substitute. The values given in Table 3.60 are the average values of the 3 determinations that were carried out for each sample. These results in Table 3.60 will be discussed in detail in Chapter 4 which now follows.

Table 3.60 : Comparison of the (average) mechanical property values for the hydrated homopolymers and copolymers.

Sample	Tensile Strength (kPa)	Elongation at Break (%)	Young's Modulus (kPa)
uncrosslinked P(HEMA)	19.9	286	13.2
crosslinked P(HEMA)	17.8	92	32.6
uncrosslinked PBA	9.5	597	6.3
crosslinked PBA	8.1	144	12.4
uncrosslinked PMA	73.3	1,436	12.0
crosslinked PMA	33.6	431	15.5
crosslinked P(HEMA-co-BA) 95:5	21.5	159	29.5
crosslinked P(HEMA-co-BA) 90:10	38.7	211	26.8
crosslinked P(HEMA-co-BA) 85:15	32.8	226	28.8
crosslinked P(HEMA-co-BA) 80:20	42.1	295	20.3
crosslinked P(HEMA-co-MA) 95:5	20.8	158	25.6
crosslinked P(HEMA-co-MA) 90:10	30.4	197	21.9
crosslinked P(HEMA-co-MA) 85:15	33.7	169	26.7
crosslinked P(HEMA-co-MA) 80:20	42.7	199	28.2