Crosslinked & Grafted Poly (vinyl chloride) with 2-Mercaptoethanol & Thiourea

Ajay Singh
Department of Chemistry, Uttaranchal University, Dehradun, Uttarakhand, 248006, India

Seema Kaval
Department of Chemistry, Uttaranchal University, Dehradun, Uttarakhand, 248006, India

Abstract- Crosslinking and grafting are useful methods for modification of common polymer like PVC. PVC is a vinyl polymer in which by dehydrohalogenation double bonds are created and crosslinking was done by using bifunctional amines. In such a way moderately crosslinked PVC possesses a high percentage of active chlorine atoms, which are good sites for reaction with sulphur nucleophiles.So in this study PVC after crosslinking with a good crosslinker like diethylenetriamine was grafted with thiocompounds. Crosslinked PVC was reacted with thiourea and 2-mercaptoethanol in order to introduce new functional groups into the polymer matrix. Polymers were characterized by fourier-transform Infrared spectroscopy (FT-IR) & thermal analysis (TGA/DTA). These modified PVC have shown good absorption capacities in different electrolytic solutions and they may find applications in different fields on the basis of their thermo mechanical and swelling behaviour.

Key words- PVC, polymer, crosslinking, absorption capacity, FT-IR, & TGA/DTA

I. INTRODUCTION

Poly (vinyl chloride), PVC is a linear polymer which is being used for replacing wood based or metal based material for the longer time. The linear materials are thermoplastic and are chemically unchanged during molding and can be reshaped again and again. Due to recent advances in polymer chemistry, the exceptions to this rule are continually growing. Crosslinking and grafting are very useful methods to modify the polymer. PVC can also be modified by crosslinking and grafting methods. Crosslinking can be initiated by heat, chemical agents, irradiation, or a combination of these. After adding various additives or by doing some chemical modifications, physical and thermo mechanical properties like tensile strength, flexibility, glass transition temperature (Tg), softening point, thermal degradation, hydrolysing character, swelling behaviour etc are altered. New functional group introduced or alteration in the original structure of the polymer change their properties and consequently modified polymers find wide applications in various fields.

In this study PVC was first crosslinked with bifunctional & trifunctional amines. Diethylenetriamine, due to its larger size and three amino groups, this amine is supposed to be a good crosslinker for PVC. Moderately crosslinked PVC may have good percentage of –Cl atoms which are good sites for reaction with nucleophiles like sulphur compounds .We selected thiourea & 2-mercaptoethanol in order to introduce new functional groups in the polymer matrix.

II. MATERIALS USED

In this study PVC has been modified by cross linking using diethylenetriamine and further crosslinked product was reacted with thiourea and mercaptoethanol to get modified polymers of PVC. Polymer PVC (Mwt-70,000) of Sigma Aldrich, diethylenetriamine, thio compounds, DMF and other reagents of German company "Merck" were used.

III. METHODS

Polymer was chemically modified in two steps, first crosslinking and then grafting.Steps are-

1. Crosslinking of PVC with DETA (c-PVC-DETA)-.In the first step, diethylenetriamine was used as a cross linker in dimethylformamide (DMF). 1.0 g of PVC was dissolved in 15 ml DMF with stirring on magnetic stirrer. After complete dissolution of polymer, 10 mL amine was added drop wise with continuous stirring. Mixture was heated at 80°C for 4 hours, to get insoluble crosslinked poly (vinyl chloride). So obtained crosslinked PVC was filtered and washed with DMF, water and methanol. This product was dried and weighed.

2. Modification of c-PVC-DETA with thiocompounds-

C-PVC-DETA (1.0 g) was stirred into DMF (10 mL) at 40°C overnight. Thiourea (2.0 g) was added and stirring was continued at that temperature for 5 hours. The polymer was filtered out and washed thoroughly with water. Reaction of the polymer with thiourea was repeated. It was then allowed to swell in DMF (15 mL) and a solution of NaOH (o.5 gm in 2mL of water) was added. The mixture was stirred at 40°C for 3 hours.The resulting polymer tested positive for the presence of thiol groups when tested with DTNB. The solid was dried and weighed to obtain 1.65 g of the product.

Modification of crosslinked PVC with 2-mercaptoethanol was done in the same manner as done with thiourea, only thiourea was replaced with 2-mercaptoethanolin this preparation. The solid was dried to obtain 1.6 g of the product.

IV. Result & Discussion

Reaction of the crosslinked polymer (c-PVC-DETA) with thiourea was applied to replace –Cl by –SH groups in a two step reaction. The reaction was a little complicated because any unreacted –Cl would react free –SH groups forming interchain or interchain sulphide links. In order to minimize such unwanted reactions, the first step of the reaction leading to isothiouronium salt was repeated to replace more unreacted –Cl atoms. Formation of charged isothiouronium groups helps greater swelling of the polymer thus exposing the unreacted –Cl groups. Another complication that arises in the oxidation of the freshly generated –SH groups to form disulphide links. The multiplicity of disulphide links forms a tight and compact 3-dimensional structure of the polymer loosing much of its utility.

PVC and its modified polymers were characterized by FT-IR (Fig- 1 to 3) and TGA/DTA (Fig-4 to 7). From the study , we observe that PVC was moderately crosslinked with diethylenetriamine at around 10% concentration at 80 °C by heating for 3-4 hours.If time , temperature & concentration of amine are increased then crosslinking increases, colour becomes darker (yellow to brownish black) and simultaneously –Cl atoms in the backbone of polymer decreases. This might be due to β-elimination of HCl molecules from PVC in strong basic medium and consequently conjugated double bonds are created in the polymer. So for further reaction of crosslinked PVC with thio-compound, active –Cl atoms should be in good percentage in the polymer. When crosslinked polymer was tested for presence of –Cl, then it gave positive test with silver nitrate solution and from its FT-IR, band at around 800 cm-1 confirms the presence of C-Cl bond in the PVC crosslinked with DETA. FT-IR spectra (fig-2) confirms the presence of C-N & N-H bonds, bands at 3310 cm-1 and around 1580 cm-1 might be corresponding to secondary N-H stretching & bending in-plane vibrations respectively and this secondary N-H bond would have been formed by elimination of HCl from reaction of NH2 group of amine and Cl atom of PVC .Other main bands in the range of 1100-1250 cm-1 might be due to C-N stretching vibrations .

Thermal stability is confirmed by thermograms shown in figure-4 to 7. Glass transition temperature (Tg) & Softening characteristics of the cross linked PVC were found to be varied than observed in PVC. Softening characteristics along with Tg are changed with the introduction of crosslinking in this polymer. Alteration and compexicity in the structure of the polymer is further confirmed by DTA curves shown in the corresponding thermograms.Glass transition temperature was observed to be lower in the modified polymer. In the study done by Biji Balakrishnan and A. Jayakrishnan,they also observed lower thermal stability for the modified polymer, in their study Poly(vinyl chloride) was aminated by treating the resin with a concentrated aqueous solution of ethylenediamine. The aminated PVC was then reacted with hexamethylene diisocyanate to incorporate the isocyanate group onto the polymer backbone. The isocyanated PVC was further reacted with poly(ethylene glycol) . The modified polymer showed the lowering of Tg the incorporation of PEG , this also supports our findings.

FT-IR of c-PVC-DETA-TU i.e., crosslinked PVC modified with thiourea is given in the figure-3. FTIR showed bands which indicated about the modification of PVC with thiocompound..The bands around 1350 cm-1 & 650 cm-1 might be corresponding to stretching vibration of C=S bond and C-S bonds. Bands around 3200 cm-1 might be due to secondary N-H stretching vibrations. Similarly modification of crosslinked PVC with 2-mercaptoethanol was also confirmed by FT-IR and Thermal analysis. Thermal stability of the modified polymer is shown in the figure 6 & 7. From the thermal graph we observed comparatively higher thermal stability of the polymer modified with thiourea (c-PVC-DETA-TU) than polymer modified with 2-mercaptoethanol(c-PVC-DETA-ME).From their DTA curves, we observe that melting of polymer modified with thiourea starts around 330°C while second modified polymer at 230°C.

Polymers modified with sulphur compounds also have shown good absorption capacity. The polymer modified with mercaptoethanol (c-PVC-DETA-ME) has better swelling properties than polymer modified with thiourea.

REFERENCES

[1] Dorel Feldman & Alla Barbalata: *Synthetic Polymers-Technology, Properties and applications, Champman* & Hall Publication, pg 5, Ed-1,(1996).

[2] Seymour,R.B and Carraher ,C.E :*Polymer Chemistry, 3rd edn*, Marcel Dekker, New York. Pg 30-38, (1996).

[3] Wilson A.S., *Plasticizers: Principles and Practice,* The Institute of Materials, Cambridge University Press, Cambridge, 1995.

[4] Faber.E., in *Encyclopedia of polymer science and Technology* Vol.13, Wiley-Intersciences,London-New York, pp 552-571.(1970).

[5] Pedro Miguel Romero et al ,*CrosslinkedPVC,* University of Alicante, Spain online 2005.

[6] Sang Phil Han et al, *Crosslinked PVC polymerization: Study on process dependencies*, PVC Research Institute, Korea ,Inc. J Appl Polym Sci 83: 1947-1954, 2002.

[7] Thai Hoang et al poly(vinyl chloride) *crosslinked by a peroxide in the presence of Trimethylolpropane trimethacrylate* Institute of Polymer Technology and Material Engineering, Loughborough University, the United Kingdom .Received on line 5-4-2003.

[8] Fiaz M. Gilbert M.: *Advances in Polymer Technology*, Vol. 17, P. 37 - 51 (1998).

[9] Biji Balakrishnan and A. Jayakrishnan ,*Chemical Modification of Poly (Vinyl Chloride) using Poly(Ethylene Glycol) to Improve Blood Compatibility* ,Trends Biomater. Artif. Organs, Vol 18 (2), January 2005.

[10] Sperling,L.H;Recent advances in polymer blends,Graft and Blocks, Plenum Press, New York (1974).

[11] .Balazs D.J et al *Surface Modification of PVC*, European Cells and Materials Vol. 6. Suppl. 1, 2003 (page 86) ISSN 1473-2262.

[12] Mascia L : *The Role of Additives in Plastics*, Edward Arnold (Publishers) Ltd.UK, (1974).

[13] Kusano, Annaka, Masahiko etal (Tokyo, JP),: *Process for producing crosslinked polymer particles* U.S Patent 4906698 ,(1995).

[14] Wendlandt W.W &.Gallagher P.K.: *Thermal Characterization of Polymeric materials*,Academic press,New York(1981).

[15] William Kemp : *Organic Spectroscopy*,IIIrd Ed.,Printed in India by Replica Press ,Kundli, page 34-37 (2004).

[16] **Ajay Singh**, M.S.M.Rawat & C.S.Pande " *Chemical* Modification and Characterization of Poly (vinyl chloride) by cross linking of multifunctional amines". *Journal of applied polymer science*". **118, issue 2**, pg 876-880, 15 Oct2010.

[17] **Ajay Singh,** M.S.M.Rawat & C.S.Pande. ".Modification, Application & Health Aspects of PVC-A Review" *Chemical Weekly*, pg195-198, 21 October, 2008.

[18] **Ajay Singh, &** M.S.M.Rawat "A Review on Poly(vinyl chloride) and its Modification by Crosslinking and Grafting" Research & Reviews in Polymer, vol.4(2),2013. Pg 73-80

Fig-1 (FT-IR of PVC)

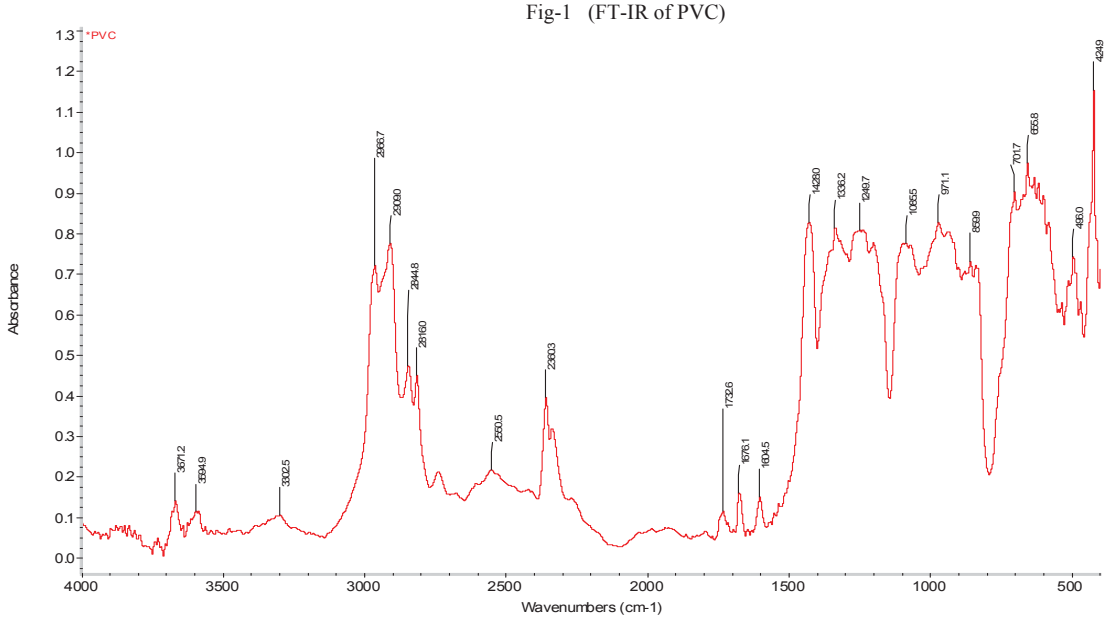

Fig –2 (FT-IR of c-PVC-DETA)

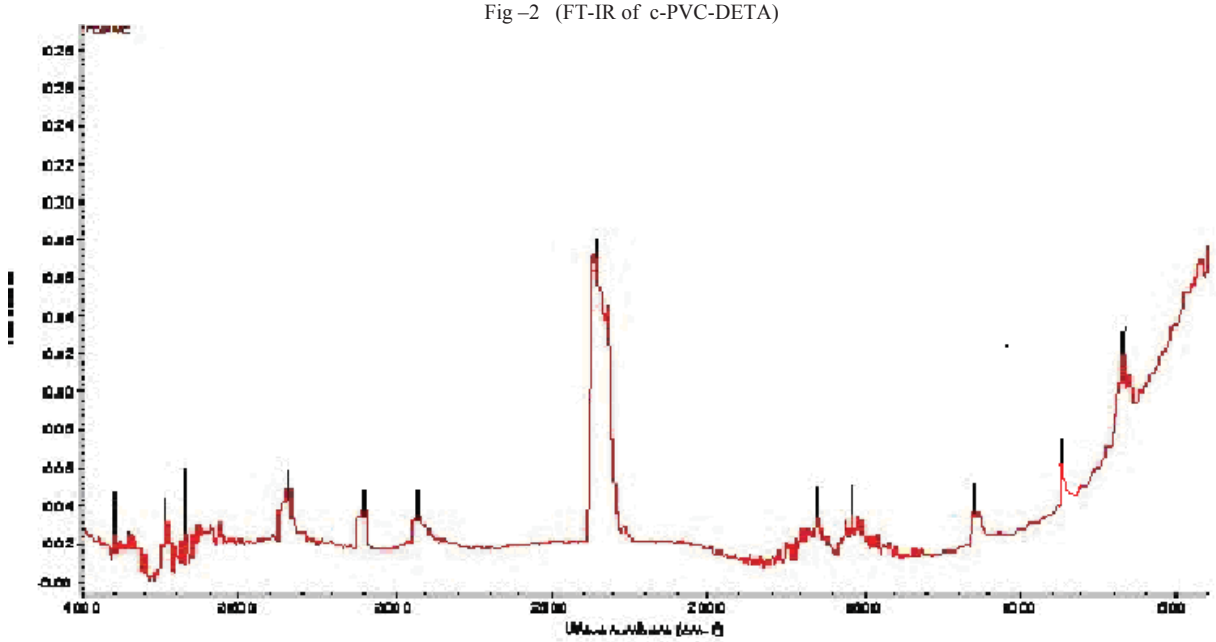

Fig. 3 (IR of c-PVC-DETA-TU)

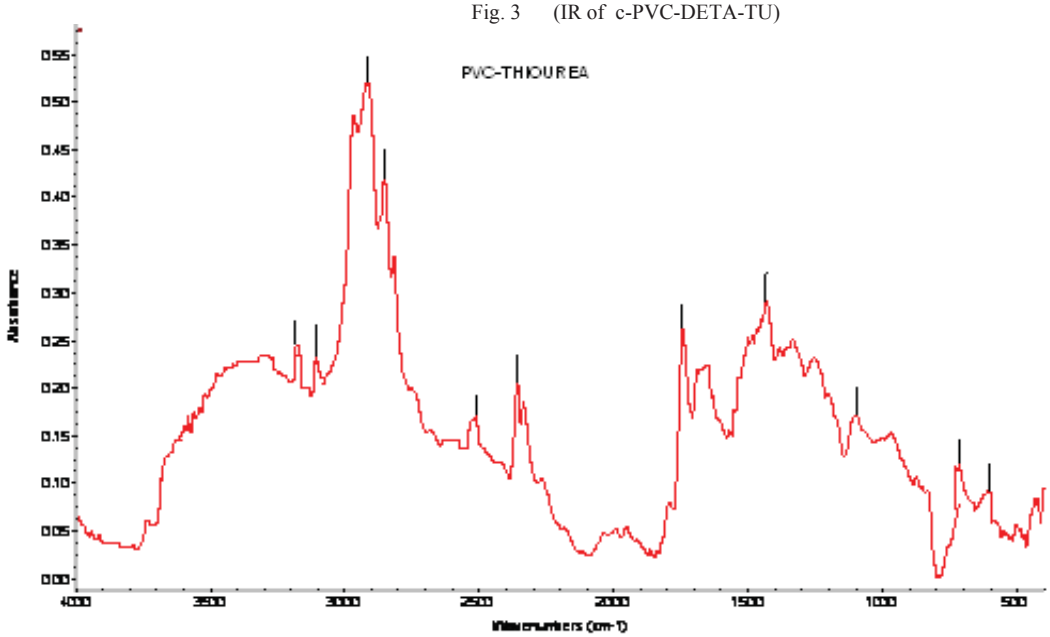

Fig.-4 (TGA/DTA of PVC)

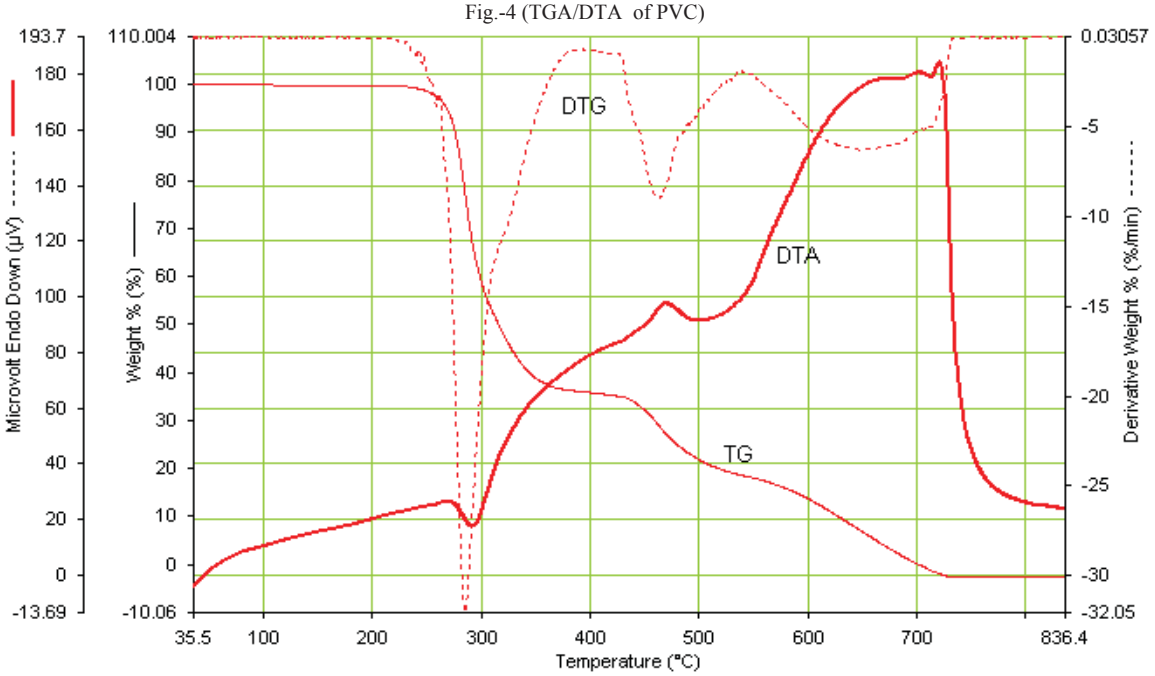

Fig-.5 (TGA/DTA of c-PVC-DETA)

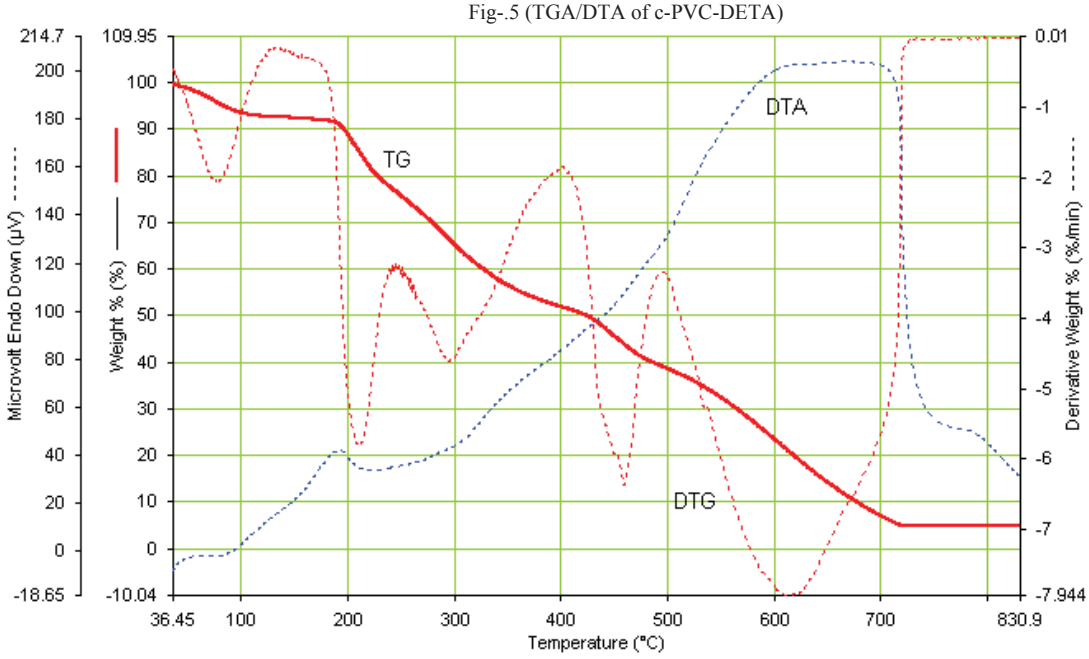

Fig- 6(TGA/DTG of c-PVC-TU)

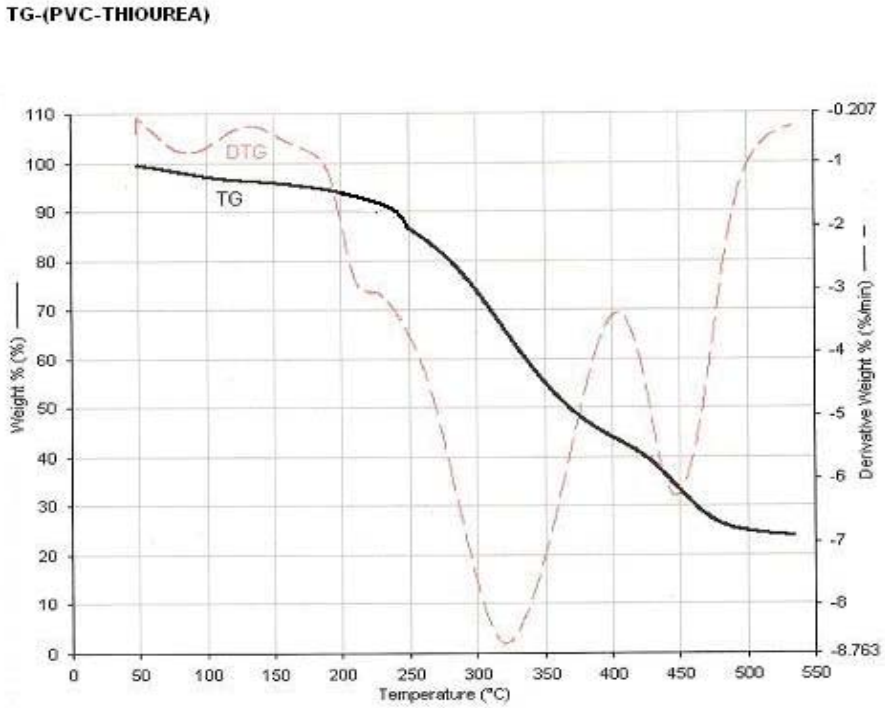

Fig- 7 (TG/DTG of c-PVC-DETA-ME)

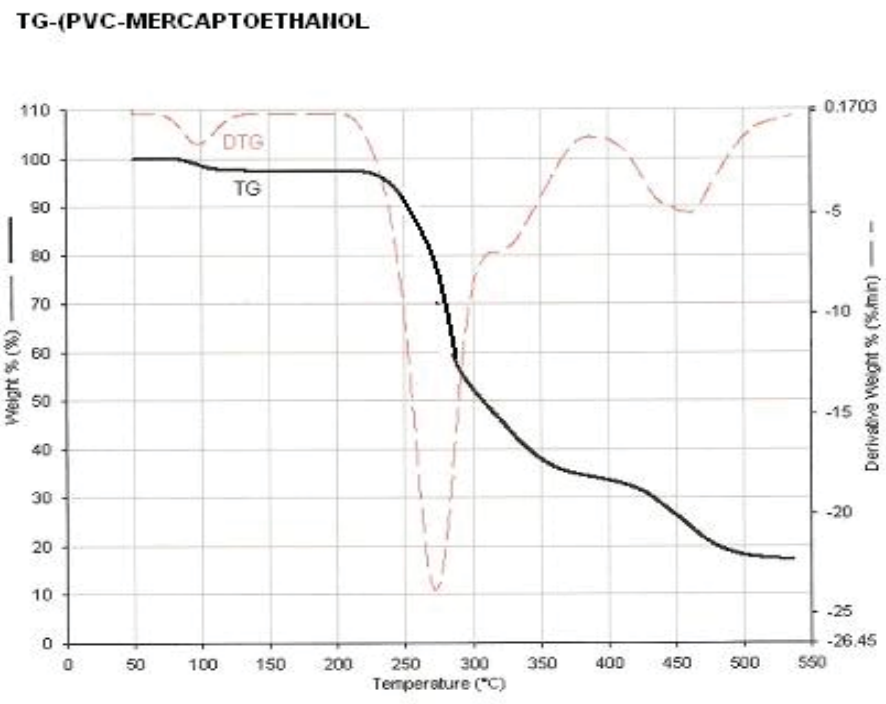

Table-1
Swelling characteristics of PVC polymers (Swelling time- 24 h)

S.No	**Polymer**	**Water** swollen by,%	**0.1N HCl** swollen by,%	**0.1N NaOH** swollen %	**0.1N NaCl** Swollen by,%
1.	PVC	8	16	12	14
2.	c-PVC-DETA	12	115	85	220
3.	c-PVC-DETA-TU	13	120	130	250
4.	c-PVC-DETA-ME	15	130	190	280

Abbreviations used-

PVC- Polyvinyl chloride

c-PVC- crosslinked PVC

DETA-Diethylene triamine

TU- Thio-urea

ME-Mercaptoethanol

TGA-Thermogravimetric analysis