

Chemical Modification and Characterization of Poly(vinyl chloride) by Crosslinking of Multifunctional Amines

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ABSTRACT: In this study poly(vinyl chloride) (PVC) was modified by using ethylenediamine, diethylenetriamine, and ethanolamine as a crosslinker in dimethylformamide. Reaction variables were optimized for getting desired crosslinked PVC, which was further reacted with maleic anhydride to form graft polymer. The anhydride group on further hydrolysis gives carboxylic group, which can exchange proton with other cations. The polymers were characterized by FTIR spectroscopy and thermal analysis (TGA/DTA).

Swelling behavior was examined in various electrolytic solutions. Modified PVC have shown good thermal stabilities and absorption capacities in neutral and acidic media, due to which these polymers might find applications in cation exchanger resin and chromatography. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 876–880, 2010

Key words: PVC; crosslinked polymer; graft polymer; FTIR; TGA/DTA; swelling behavior

INTRODUCTION

Poly(vinyl chloride), commonly abbreviated PVC, is a widely used thermoplastic polymer. In terms of revenue generated, it is one of the most valuable products of the chemical industry. In recent years, PVC has been replacing traditional materials such as wood, concrete, and clay in many areas. Despite claims that PVC production negatively affects the natural environment and human health,¹ it is widely used as a hard plastic in magnetic strip cards, window profiles, gramophone records, plumbing, and pipes in the water and sewer industries whereas, as a soft plastic in packaging bags, blood solution bags, dialysis devices, catheter, bottles, etc.² Because of —Cl side groups; it becomes amorphous, hard, and brittle. Presence of chlorine atoms in PVC hinders burning through formation of incombustible HCl and reacts with free radicals generated during combustion and acts as terminator for the combustion propagation reactions. Thus, by virtue of its chemical nature PVC achieves the kind of flame retardancy, which is generally not found in other plastics.^{3,4} In this way PVC gets advantage over other plastics. As such PVC has limited uses but by adding different additives like plasticizers (phthalates) or by doing some chemical modifications its thermo-mechanical properties can be modified up to desired

extent. Crosslinking and grafting are very useful techniques for the modification of polymers. Crosslinking can be initiated by heat, chemical agents, irradiation, or a combination of these.⁵ Theoretically, any linear plastic can be converted into a crosslinked plastic with some modification in the molecule.^{6,7}

In this study PVC was first modified by crosslinking with multifunctional amines and then that crosslinked product was reacted with maleic anhydride to get additional modified polymer. During the process some of the —Cl atom are eliminated in the form of HCl molecules to produce double bonds in the polymer chain, which seems to be similar to the dehydrohalogenation of alkyl halides. The unsaturated polymer so formed reacts with maleic anhydride to form the graft polymer. The reaction is almost similar to the Diels-Alder addition reaction.

EXPERIMENTAL

Materials

Polymer PVC (Mwt-70,000) of Sigma Aldrich (Fluke, St. Louis, MO); ethylenediamine, diethylenetriamine, and ethanolamine of Merck (Germany); dimethylformamide of Merck (Germany); methanol, HCl, NaCl, and NaOH of Ranbaxy (India) were used.

Instruments

Infra red spectra of the polymer samples were recorded as KBr pellets in cm^{-1} on RX₁ Perkin-Elmer FTIR instrument. Thermal analysis of polymer

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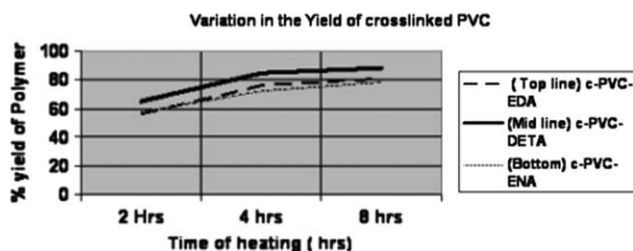


Figure 1 % Variation in the yield of polymers (at 10% PVC and 20 %amine conc.).

samples was done by using Prism diamond Perkin-Elmer thermal analyzer. Nitrogen (N₂) was used as purging gas and temperature was increased at the rate of 10°C per minute.

METHODS

PVC was modified in two steps, first crosslinking and then by grafting or addition reaction. In the first step, ethylenediamine, diethylenetriamine, and ethanolamine were taken as a crosslinker in the solvent dimethylformamide (DMF). One gram of PVC was dissolved in 10 mL of DMF at 40°C with stirring on magnetic stirrer. Concentration of PVC in DMF was varied between 5 to 20%. After complete dissolution of polymer, amine was added dropwise with continuous stirring to get 20% amine concentration in the reaction mixture (v/v). Temperature was raised from 40 to 80°C and reaction mixture was heated for 4–5 h to get insoluble crosslinked PVC. Reaction variables (time, temperature, and concentration) were optimized to get the desired crosslinked product. Reaction time of about 4 h at 80°C was sufficient to get the crosslinked yield of about 80%. The products were filtered with the help of preweighed sintered glass crucible and washed with DMF, water, and finally with methanol, dried and weighed.

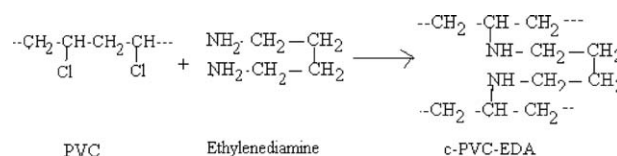
In the second step of modification, 1 g of crosslinked product obtained as in first step was allowed to swell in 20 mL DMF for about 2 h at 30°C temperature and then reacted with 0.5 g of maleic anhydride at 50°C for 1 h. Thus obtained product was given the treatment of HCl followed by alkali and finally the product was filtered, washed, and dried.

RESULTS AND DISCUSSION

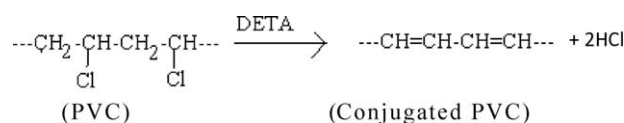
In this study, first reaction conditions were optimized by varying the temperature, time of heating, and concentration of polymer in the solvent to get more than 75% yield of crosslinked product. Results have been graphically presented in Figure 1. From this figure it is clear that maximum yield of the crosslinked product of PVC was obtained by heating at 80°C for 4–5 h at 10% (w/v) polymer concentra-

tion and 20% (v/v) amine concentration in the solution. Obtained product was observed yellow to dark brown in color. In the subsequent study, this color was reduced to lighter by treatment of maleic anhydride. The crosslinked products were characterized with the help of FTIR and thermal Analysis (TGA/DTA). FTIR spectra of some polymers are shown in Figures 2–5 and thermal analysis curves are shown in Figures 6–9. Elemental analysis of the polymer samples (Nitrogen and Chlorine content) by XRD method is given in the Table I. Some probable reactions of formation of modified PVC with amines and maleic anhydride have been summarized in scheme as given:

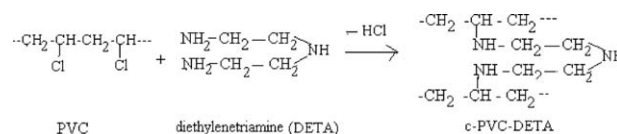
Reaction of formation of crosslinked PVC with ethylenediamine:



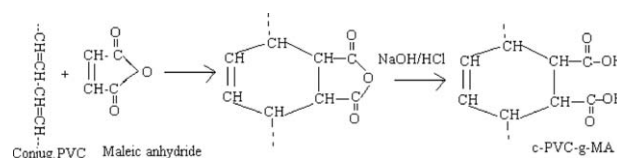
Probable reaction of formation of conjugation in PVC in presence of concentrated amine (DETA):



Probable reaction of PVC with diethylenetriamine given as:



Probable reaction of the formation of addition product through Diels-Alder reaction follows as:



After the analysis of results, it can be concluded that PVC could be better crosslinked with diethylenetriamine at around 10% concentration of PVC in DMF at 80°C. Because of its larger size and three amino groups, this amine is supposed to be a good crosslinker reagent for PVC. Bands at 3310 and 1580 cm⁻¹ (Fig. 4) might be corresponding to secondary N–H stretching and bending in-plane vibrations,

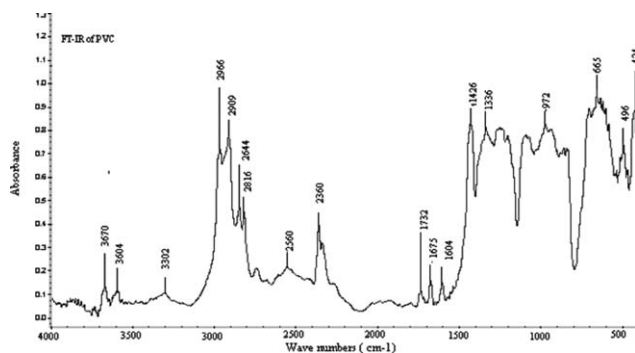


Figure 2 FTIR of PVC.

respectively, which confirm their presence. Secondary N—H bond would have been formed by elimination of HCl from reaction of NH_2 group of amine and —Cl atom of PVC. Other main bands in the range of $1200\text{--}1360\text{ cm}^{-1}$ might be due to C—N stretching vibrations. Similarly other bands in the FTIR spectra 3 to 5 support the crosslinking in the polymer with other amines. By XRD analysis of polymers given in Table I it is clear that chlorine content in the c-PVC-DETA is minimum i.e., 3.2%, whereas 3.8% in c-PVC-EDA when compared to 56.4% in original PVC. Nitrogen content is maximum about 22.3% in c-PVC-DETA followed by 16.8% in c-PVC-EDA, which indicates the substitution of maximum chlorine with nitrogen compounds and consequently it supports that. PVC has been best crosslinked with diethylenetriamine followed by ethylenediamine. On comparing the TGA curves (Figs. 6–9) thermal stability was observed to be lowered for the modified polymers. Thermal stability and softening characteristics along with T_g (glass transition temperature) were observed to be altered when compared to original PVC for all the three new polymers with the introduction of crosslinking in the polymer. Polymers are hard and glassy below T_g , rubbery above T_g . In this way original properties get modified and a new product of polymer is obtained. The polymer crosslinked with ethanolamine (c-PVC-ENA) was found to have greater ther-

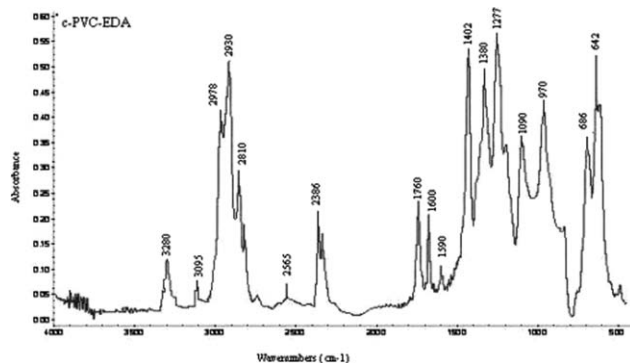


Figure 3 FTIR of c-PVC-EDA.

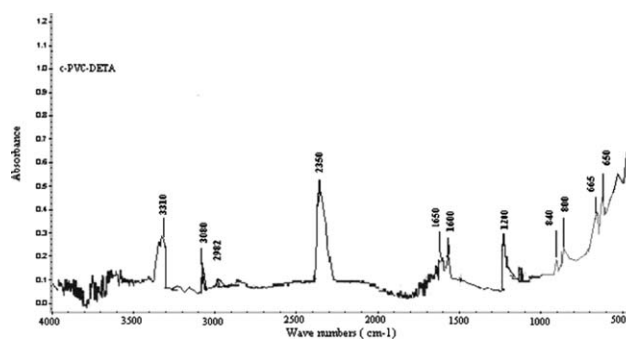


Figure 4 FTIR of c-PVC-DETA.

mal stability than other crosslinked polymers, whereas in ethylenediamine crosslinked product (c-PVC-EDA) was found to have comparatively lower thermal stability. Generally by introduction of crosslinking in the polymer, thermal stability is supposed to increase,⁸ but in some cases, it can decrease.⁹

In our study we observed yellowish to brownish crosslinked products. Intensity of color of the crosslinked product was found to increase with the increase of heating time and temperature. Color of the polymer may be due to generation of new double bonds or conjugation in the polymer by elimination of HCl molecules. There is possibility of β -elimination reaction in basic medium similar to dehydrohalogenation of alkylhalides in strong alkaline medium.¹⁰ Elimination of HCl molecules becomes more prominent as time and temperature are increased. More elimination is also supported by the gradual decrease in the pH of the medium with the progress of the reaction. Some dark color may be due to oxidation of extra added amines at higher temperature. This fact is further supported by the study of Romero et al.⁵ This study revealed that crosslinking reactions promoted thermal degradation phenomenon in the polymer matrix. This is attributed to the formation of HCl and other species promoting polymer degradation during crosslinking,

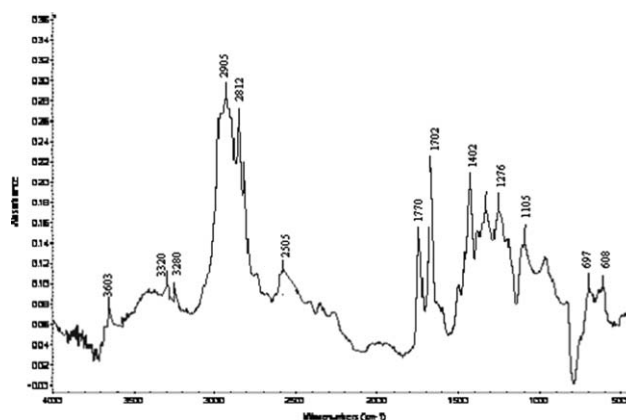


Figure 5 FTIR of c-PVC-MA.

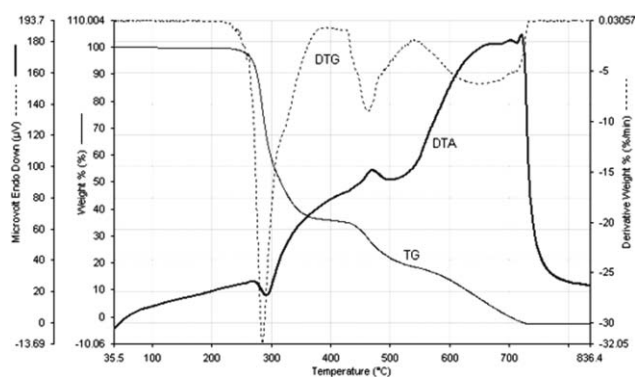


Figure 6 TGA of PVC.

the result is further supported by another study of Han et al.⁶

In the subsequent study, the best crosslinked PVC i.e., crosslinked with DETA (c-PVC-DETA) was reacted with maleic anhydride to get a new additional product. The addition product with lighter color was obtained due to the addition via Diels-Alder reaction, which decrease the degree of unsaturation. This decrease in conjugation resulted in the reduction of color of the product. This is further supported by FTIR spectra shown in Figure 5. Thermal stability of the addition product (c-PVC-g-MA) was observed to be increased (Fig. 9), this might be due to introduction of carboxylic group in the polymer, which may provide the hardness to the polymer. H^+ of the carboxylic group might be exchanged with other cation to behave like cation exchanger.

Swelling characteristics of the polymer-absorption capacities of the various modified polymers and PVC were determined in neutral water, *N*/10 HCl, *N*/10 NaOH, and *N*/10 NaCl solutions for 8 and 24 h. Results have been given in Table II, which showed that grafted polymer of crosslinked PVC with anhydride (c-PVC-g-MA) had maximum absorption capacity of about 270% (in 24 h) in salt solution followed by PVC crosslinked with diethylenetriamine(c-PVC-DETA) having swelling capacity of about 220%. Acid solution grafted polymer has

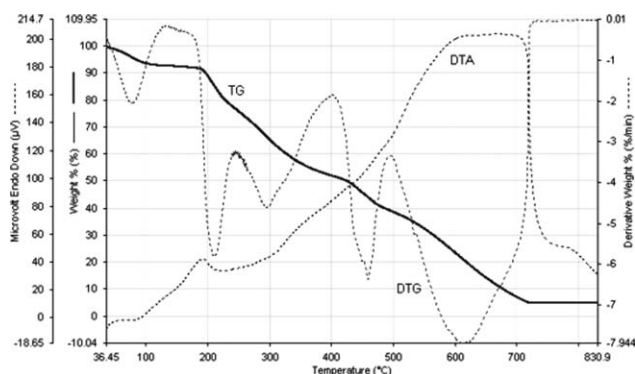


Figure 7 TGA of c-PVC-DETA.

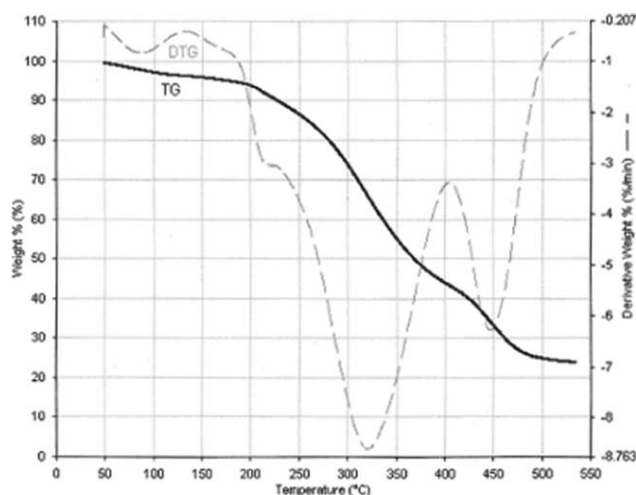


Figure 8 TGA of c-PVC-ENA.

shown maximum absorption of about 150% followed by PVC crosslinked with ethylenediamine(c-PVC-EDA) i.e., 130%. In alkaline solution also, grafted polymer has shown maximum absorption of about 115%. Maximum absorption capacities of modified polymers were observed in the *N*/10 NaCl salt solution.

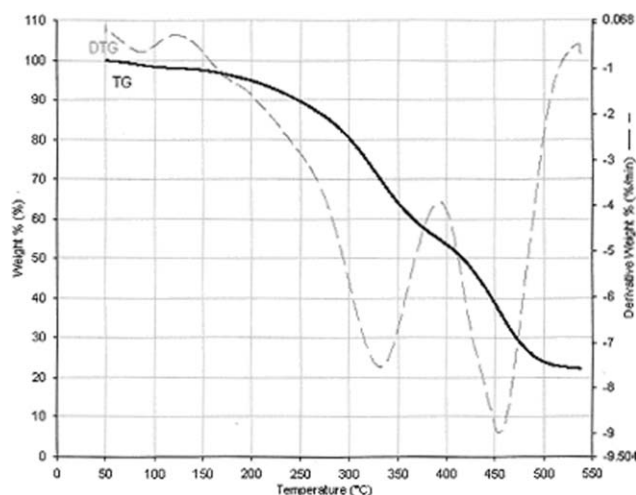


Figure 9 TGA of c-PVC-MA.

TABLE I
Nitrogen and Chlorine Contents in the Polymer Samples
(By XRD Method)

Polymer	% N (Nitrogen content)	% Cl (Chlorine content)
PVC	0	56.4
c-PVC-EDA	16.8	3.8
c-PVC-DETA	22.3	3.2
c-PVC-ENA	11.8	4.2

c, crosslinked; EDA, Ethylenediamine; DETA, Diethylenetriamine; ENA, Ethanolamine.

TABLE II
Swelling Characteristics of the Polymer Samples (Swollen Time 8–24 h)

Polymer	Water % absorption	0.1N HCl % absorption	0.1N NaOH % absorption	0.1N NaCl % absorption
PVC	4–8%	10–16%	8–12%	10–14%
c-PVC-EDA	8–12%	80–130%	62–90%	120–170%
c-PVC-DETA	9–12%	70–115%	56–85%	140–220%
c-PVC-ENA	14–20%	68–105%	65–95%	130–200%
c-PVC-g-MA	15–22%	110–155%	75–115%	160–270%

1st and 2nd value corresponding to 8 and 24 h swelling time, respectively.
MA, Maleic Anhydride; g, grafted.

Applications of any polymer depend upon its thermal stability, swelling behavior, and the type of modification introduced in the molecule. In a recent study⁵ it was shown that grafting of poly (ethylene glycol) (PEG) onto PVC surface by the well known Williamson reaction can generate a protein and platelet repelling surface. Although surface modification is the key to altering the surface properties of the polymer without changing its physical and mechanical properties. Most of the PVC-based devices used for medical applications fall into this category. Introduction of sophisticated chemical structures on the backbone of the polymer chain prior to processing is resorted to many cases to produce the final product with the required physical, chemical, and biological properties.¹¹ Similarly in this study PVC was crosslinked to produce desired level of unsaturation so that addition of maleic anhydride could be done easily to graft carboxylic group in the backbone structure of PVC.

CONCLUSION

In this study, two main findings were observed. In the first finding, PVC could be better crosslinked with diethylenetriamine (c-PVC-DETA) than any other amine and more than 80% yield was obtained by heating for 4 h at 80°C. In the subsequent study,

crosslinked PVC (c-PVC-DETA) was grafted with carboxylic group by reacting with maleic anhydride. Carboxylic group is capable of exchanging H⁺ ions and this property might be used as cation exchanger. The grafted polymer (c-PVC-g-MA) has shown good absorption capacities in different electrolytic solutions, so it might be used as hydrogels in various applications like in chromatography.

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