



Synthesis, Characterization and Viscometric Study of Carboxymethyl Epoxy Resin Based Polyesters

KEYWORDS

Polyelectrolyte, CMPE, reduced viscosity, empirical relation and intrinsic viscosity

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ABSTRACT Viscometric study of solutions of various carboxymethylated epoxy resin based polyesters in 1,4-dioxane solvent was carried out. Measurement was performed using Ubbelohde suspended type viscometer. The viscosity for all CMPE solutions were determined in 1,4-dioxane at 30 ± 0.1°C. The viscosity data of all solutions suggest the decrease in concentration of solution which increases reduced viscosity (η_{red}). Therefore the CMPE resins act as polyelectrolyte of anionic type. The viscosity of the solution in 1,4-dioxane suppressed by adding water and KBr, though the intrinsic viscosity measurements are carried out for all resin solutions in Dioxane-Water-KBr having 75:25:1% ratio. Also empirical equation was adept to represent the viscometric data for all the resins. It may be stated that as the equation is quite empirical. $\eta_{sp}/c = z - [\eta] + \frac{k[\eta]^2}{c}$

Introduction:

Polyelectrolytes are polymers carrying positive or negative charged ionizable groups on their repeating units. The properties of this polyelectrolyte in solutions and at charged surfaces depend on the dissociated ionic groups, quality of solvent, dielectric constant of solution and polymer-substrate interactions [1-3]. Both the repulsive and electrostatic interactions between ionizable groups represent leading factors which influence the behavior of polyelectrolytes in solution. The amphiphilic polyelectrolytes, exhibit solution properties arise from the competition between the hydrophobic and electrostatic interactions [4,5]. These interactions are strongly sensitive to some parameters, like: the chain length, the charge density, the polyelectrolyte concentration, the counter ion type, the ionic strength, the solvent polarity, the length and content of hydrophobic groups, etc [6-8]. In addition, both interactions known for its important role in biological systems, technology field as well as in environmental aspects [9-11]. The numerous experimental methods have been reported for the behaviour of polymers in the solid state and in solution, amongst them viscometry used widely due to its effortless and reliable nature [12-14].

In our earlier communication [15] we reported the viscometric study of CMPEs in DMF solvent. In continuation of previous work the present communication comprises the viscometric study of carboxymethylated epoxy-resin polyester resins using 1,4-dioxane as a solvent.

Experimental:

Materials:

Epoxy resin based polyester resin used was reported in our earlier communication [15]. All of the chemical used were of analytical grade. The viscometer bath was used with maintaining temperature 30 ± 0.1°C.

Measurements:

C, H, N analyses (Table-1) were carried out by Colman Analyzer. The infrared spectra (FT-IR) were obtained from KBr pellets in the range 4000–400 cm⁻¹ with a Perkin Elmer spectrum GX spectrophotometer (FT-IR) instrument. The

thermogravimetric analysis of CMPEs was carried out by Du Pont 950 thermogravimetric analyzer at 10°K per minutes.

Table-1: Characterization of CMPE resin

Polymer sample	Functional group	Mol. Wt.	Elemental analysis (%)			
			C		H	
			Calc.	Found	Calc.	Found
CMPE-1	-	539	64.56	64.44	5.79	5.71
CMPE-2	-CH ₂	592	65.09	65.01	6.01	5.94
CMPE-3	-(CH ₂) ₂	606	65.60	65.52	6.22	6.15
CMPE-4	-(CH ₂) ₄ -	634	66.45	66.39	6.60	6.52

The relative, specific and reduced viscosity of the CMPE resin solutions from the flow times of solutions was measured by using the Ubbelohde capillary viscometer. The viscosity measurements were carried out at a constant temperature of 30 ± 0.1°C. The temperature of solution was controlled by a thermostat in a circulating bath and monitored by the thermometer. A stopwatch with a resolution of 0.1s was used to measure the flow times. By plotting the reduced viscosity (dL/g) of polymer solutions against concentration (g/dL), extrapolating to infinite dilution and taking the intercept, the intrinsic viscosity $[\eta]$ is determined.

Table-2: Reduce viscosity of solution of CMPE resin using 1,4-Dioxane.

Polymer Samples	Reduced Viscosity (η_{red} dL/g) at concentration, (C g/dL)				
	3.000	2.142	1.666	1.363	1.152
CMPE-1	0.09357	0.09250	0.0935	0.0960	0.09830
CMPE-2	0.11825	0.11609	0.11740	0.11932	0.12864
CMPE-3	0.10659	0.10401	0.10808	0.11475	0.11953
CMPE-4	0.08090	0.08193	0.08345	0.08950	0.09183

Table-3: Reduce viscosity of solution of CMPE resin using Dioxane-water-KBr (75:25:1%).

Polymer Samples	Reduced Viscosity (η_{red} dL/g) at concentration, (C g/dL)					Intrinsic Viscosity [η] $\times 10^2$	Slope of linear plot $K \times 10^3$
	3.000	2.142	1.666	1.363	1.152		
CMPE-1	0.08356	0.08024	0.07851	0.07609	0.07511	7.87	4.55
CMPE-2	0.10051	0.09828	0.09707	0.09495	0.09237	9.66	4.00
CMPE-3	0.08669	0.08448	0.08312	0.08234	0.08160	8.36	2.73
CMPE-4	0.06120	0.05974	0.05891	0.05842	0.05860	5.93	1.52

Table-4: Reduce viscosity of solution of CMPE resins using 1,4-Dioxane.

Polymer Samples	Reduced Viscosity (η_{red} dL/g) vs $1/C^{1/2}$					Intrinsic Viscosity [η] $\times 10^2$
	0.577	0.683	0.774	0.856	0.931	
CMPE-1	0.09357	0.09250	0.0935	0.0958	0.09830	9.47
CMPE-2	0.11825	0.11609	0.11740	0.11932	0.12864	11.99
CMPE-3	0.10659	0.10401	0.10808	0.11475	0.11953	11.05
CMPE-4	0.08090	0.08193	0.08345	0.08950	0.09183	8.55

Figure-1: Reduced Viscosity vs Concentration of CMPE resins using Dioxane.

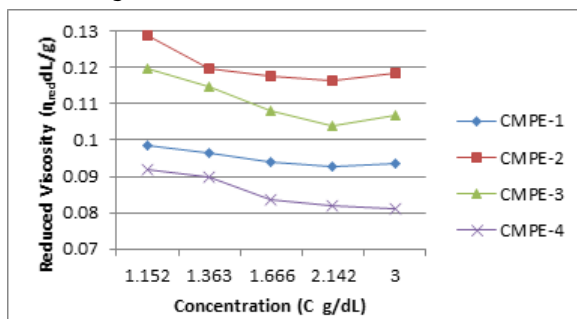


Figure-2: Reduced Viscosity vs Conc. of CMPEs/Dioxane-water-KBr (75:25:1%).

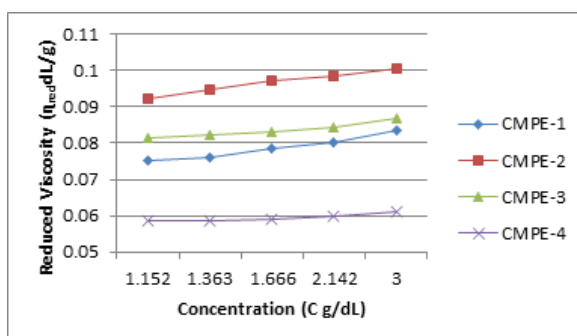


Figure-3: Reduced Viscosity vs $1/C^{1/2}$ of CMPE (Applica-

tion of empirical relation).

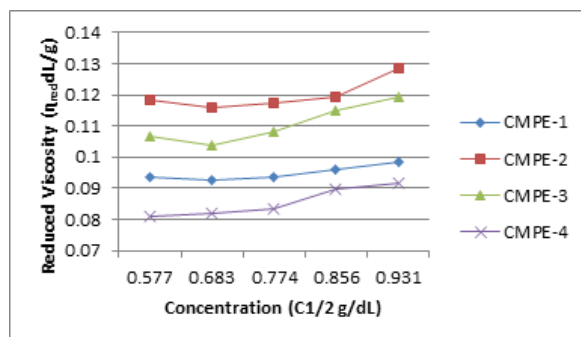
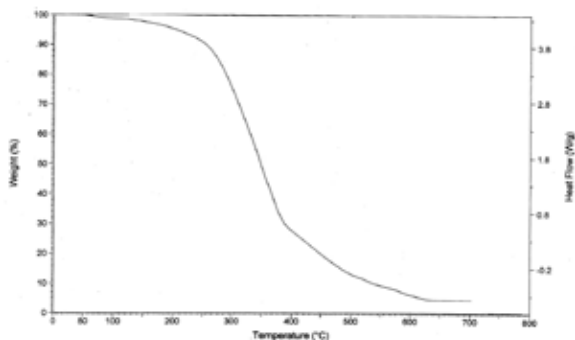


Figure-4: IR spectrum of CMPE-1



Figure-5: TG spectrum of CMPE-1



Results and Discussion:

All the four resins i.e. CMPE 1 to 4 were in form of amorphous powder. The C, H and N contents of all four CMPEs are consistent with their predicted structure [15]. Their details are furnished in Table-1. The IR spectra (Figure-4) of all the resins are almost identical in shape and intensity of bands. All the polymers show bands at around 3420 cm^{-1} for -OH stretching. Also the characteristic bands for aromatic stretching at around 3030 cm^{-1} , Assymmetric -CH₂ stretching at around 2930 and C-O-C linkage around 1200 cm^{-1} support the structure of polymers. Only discernible band are 1720 cm^{-1} is responsible to -COOH group.

Examination of the TG curves (Figure-5) of polymer samples reveals that each of them degrades in two steps. The first stages of degradation up to 230° to 250°C of all the polymers indicate the weight loss at 10 to 12% percentages. This is depending up on the molecular weight of sample. All the polymers containing one -COOH groups, hence the TGA of polymers in air may cause decarboxylation. The calculated value of CO₂ of each polymers and % loss of degradation of each polymers reveals that the decarboxylation of each polymer consistent with the calculated values. Furthermore, degradation becomes faster

between 300°C - 400°C and 60% weight loss observed in this range. The weight loss was about 90% at 630°C in all cases. All these facts support the structure of polymers.

The reduced viscosity of the CMPE resin solution in to the Dioxane solvent is shown in **Figure-1** as the function of polymer concentration. It is seen from the **Figure-1** that the reduced viscosity increases with the decreasing polymer concentration. This typical polyelectrolyte behavior like this for the reason that the carboxylic groups on the polymer chain can ionize in the polar solvent and also the effective electrostatic repulsion makes this polymer chain highly extended [16,17]. In this case measurement could not be performed at sufficiently low concentrations owing to the comparatively low viscosity of these solutions. The polyelectrolyte either cationic or anionic polymers have special viscosity behavior in association with neutral polymer. Neutral polymers have the properties that reduce viscosity increases with the increase of polymer concentration.

The effort was finished to determine the viscosity in mixed form of Dioxane and water/KBr (75:25) solvent system. The results are also parity to neat solvent. This may caused by addition of water the ionization of polyelectrolyte decreases due to the dielectric constant. The dielectric constant has a significant effect on the strength and range of electrostatic interactions [18,19].

Figure-2 shows the Reduced viscosity as a function of polymer concentration in the presence of Dioxane-water-KBr (75:25:1%). The mechanism of the KBr effect on reducing the polyelectrolyte effect mainly is related to the reduction of double layer thickness on the polyelectrolyte molecule. Due to high degree of ionization, KBr reduces the partial ionization of polyelectrolyte and eliminates the polyelectrolyte effect at lower concentration. When small molecule electrolyte is added to the polyelectrolyte solution depending on the concentration, the viscosity behavior changes [20]. It is seen from **Figure-2** that there is not electrolyte effect and viscosity does not increase with decreasing polymer concentration, which is in contrast with salt-free solution.

Viscosity of a given solution of a rigid polymer depends upon the interactions between the polymer chain and upon the hydrodynamic volume of the polymer. In the present case the solution contains a polycarboxylate ion. Because of lower shielding of the COO⁻ ions present in the polymer chains, the polymer chains will keep away from each other to minimize the repulsive interaction. With increase in dilution, the number of solvent molecules per molecules of polymer chain would increase. Hence number of solvent molecules surrounding each ion on polymer chain would increase. The repulsive interaction of polymer chain would decrease. Due to association of COO⁻ with larger number of solvent molecules the hydrodynamic volume would also increase. With increase in dilution the strength of repulsive interaction decreases and the hydrodynamic volume increases. As a result the viscosity functions would increase with decrease in concentration of polymer solutions.

In case a circumstance is produced such that, (i) The negatively charged ion is well surrounded by an equal number of both +ve and -ve ions, the polyelectrolytic behavior will not be observed. This situation is created by adding a strong electrolyte to the solution in which the viscometry is carried out. (ii) The negatively charged ions of the poly ionic species are very well solvated even in concentrated solution to the

extent that, on further dilution there is no additional solvation or protection. This situation is created by increasing the solvent power of the solvent e.g. by using a mixture like Dioxane – water mixture as solvent in place of a pure solvent.

Application of empirical relation to the data:

The empirical relation is, $\eta_{sp}/C = Z + \frac{K[\eta]}{C^{1/2}}$

The application of the equation to the data has been examined and the results are represented in the **Table-4**. The plots are shown in **Figure-3**; this was indicated that the plots were linear. From the plots, values of intercept $[\eta]$ and K were appraised. These constants are presented in **Table-4**. The above mentioned empirical equation is able to represent the empirical data for all the polymers. It may be stated that as the equation is quite empirical, no significance can be attached to the definition of the intercept which follows from the equation.

Conclusion:

The present study deals with the different viscometric measurements of carboxymethyleted epoxy resin based polyesters using 1,4-dioxane solvent. The intrinsic viscosity has been determined by extrapolating the reduced viscosity to zero concentration. The effects of solvent Dioxane and solvent-water-KBr on viscosity have been investigated. The reduced viscosity of CMPE solutions in dioxane results into the polymer chain expansion with decreasing polymer concentration, which further suggest that the polymer behaves like a polyelectrolyte in salt-free solution. The use of water into the solvent results into the decreases the reduce viscosity, while addition of small amount of low molecular weight electrolyte (KBr) removes the polyelectrolyte effect of polyester. So the polyester behaves like a neutral polymer which is further supported by decrease in the viscosity with decrease in the polymer concentration.

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