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Determination of Iodine Value of Certain Polymers Using Chloramine-T as Reagent

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Chloramine-T (CAT) has been used as the analytical reagent for the determination of iodine value of certain polymer samples. The simple titrimetric method involves the treatment of polymer solution with an excess of CAT in the presence of glacial acetic acid (GAA), where quantitative addition of CAT to the olefinic bonds of the polymer takes place. The unreacted CAT was determined iodometrically.

INTRODUCTION

The iodine value of a polymer is a measure of the degree of unsaturation. The chemical, viscoelastic and rheomechanical properties of the polymers depend upon the reactivity of the total double bonds and the type of neighbouring groups present. Hence, the determination of the iodine value is of industrial importance. In literature, various methods are available but three methods are commercially employed. The Wij's method involves the use of iodine monochloride in glacial acetic acid media.[1] The Hanu's method employs iodine monobromide in glacial acetic acid[2], and in Kaufmann method, a solution of bromine and sodium bromide in methanol is being used.[3]

Chloramine-T (CAT) is an efficient reagent because of its versatile chemical reactivity and diverse nature.[4–6] It has been found to be useful for the measurement of the degree of unsaturation of oils, fats and other organic molecules.[7] It has not been used for the determination of iodine values of polymers. Hence, a simple titrimetric method has been developed to determine the iodine value of certain industrially important polymers.

EXPERIMENTAL

AnalaR grade reagents were used in these experiments Solvents were used after distillation. CAT (CDH, Mumbai) was purified by the method of Morris *et al.*[8] A solution of CAT in glacial acetic acid was prepared, standardised periodically by the iodometric method, and preserved in an amber coloured bottle until further use. Double distilled water was used for the preparation of sodium thiosulphate and potassium iodide solutions. Five polymers namely natural rubber, polybutadiene, styrene butadiene copolymers of composition (66 : 34) and (34 : 66), and butyl rubber obtained from M/s. Vikrant Tyres, Mysore were analysed.

Procedure

A known quantity of the polymer was accurately weighed into a clean and dry iodine flask and dissolved in the appropriate solvent (Table-1). 50 mL of CAT solution (0.25 eqv. dm^{-3}) was added and the resulting solution was agitated slowly using a mechanical shaker for 90 min. After the completion of the reaction, 10 mL of 10% potassium iodide solution and 50 mL of 1 mol dm^{-3} sulphuric acid solution were added. The liberated iodine was titrated with sodium thiosulphate solution (0.1 eqv. dm^{-3}). A blank experiment was carried out under identical conditions except the polymer sample. The iodine value was obtained from the following relation.

$$\text{Iodine value} = \frac{(V_2 - V_1)12.69\ n}{m}$$

where V_1 and V_2 are the volumes of sodium thiosulphate solution used for sample and blank titrations respectively,
n is strength of thiosulphate solution in eqv. dm^{-3}, and
m is mass of the polymer sample in g.

The results obtained are presented in Table-1.

TABLE-1
IODINE VALUE OF POLYMERS

Sample (Solvent)	Experimental value*						Average values (Standard deviation)	Literature Value (Wij's Method)
	1	2	3	4	5	6		
Natural Rubber (chlorobenzene)	360.18 (110)	360.60 (125)	360.20 (132)	360.64 (148)	360.19 (149)	360.30 (160)	360.35 (0.2)	345–375 (360.5)
Polybutadiene (benzene)	407.5 (107)	407.9 (127)	408.1 (102)	407.3 (120)	407.9 (143)	408.2 (155)	407.8 (0.31)	385–440 (408.7)
Styrene-butadiene copolymer (66 : 34) (chlorobenzene or ethyl acetate)	129.2 (90)	129.6 (110)	129.8 (115)	129.5 (116)	129.9 (126)	130.0 (190)	129.66 (0.27)	*ca.* 140 (130.8)
Styrene-butadiene copolymer (34 : 66)	258.5 (101)	258.1 (110)	259.0 (126)	258.3 (129)	258.6 (127)	258.9 (139)	258.56 (0.31)	*ca.* 290 (259.2)
Butyl rubber (Chloroform)	3.52 (190)	3.8 (210)	4.0 (220)	3.92 (201)	3.68 (223)	3.4 (230)	3.72 (0.21)	< 5 (3.6)

RESULTS AND DISCUSSION

In the presence of glacial acetic acid CAT adds quantitatively to the —C=C— bond resulting in the acetoxy (chloro) alkane or tosylamino (chloro) alkane.[9]

The overall reaction involves the addition of one mole of CAT per —C==C— unit which in turn is equal to one mole of iodine.

As a typical comparison the iodine values were also determined by Wij's method. The results of the two methods compare well with each other and found to be within the range of literature values.[3]

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