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A STUDY ON UV-VISIBLE SPECTROCOPY AND X-RAY DIFFRACTION OF THE INTERACTION OF NR AND PEO BASED BLOCK COPOLYMERS WITH CATIONIC DYES

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ABSTRACT

A series of block copolymers were prepared from polyethylene oxide (PEO) of varying molecular weigh and hydroxy terminated liquid natural rubber (HTNR) by solution polymerization. Two phase morphology of these block copolymers was confirmed by analytical means[1]. The inherent property of PEO to complex with cationic dyes is shown by the NR/PEO block copolymer. The block copolymer thus show appreciable absorption of the three cationic dyes, viz., malachite green (MG), safranine T (ST) and methylene blue (MB). The spectral studies on the virgin copolymer and the dye stained copolymer show that the dye solutions interact with the PEO segments of the copolymers indicated by a hypsochromic shift. XRD shows that cationic dye complexation does bring about significant changes in the crystallinity of the block copolymers.

Key words: PEO, HTNR, XRD, Block copolymers.

INTRODUCTION

The influence of scientific and technological advancements, rapid advances in synthetic strategies and the necessity of materials with sophisticated and wide applications urged the need of developing modified polymers like polymer blend, composites, interpenetrating networks (IPNs) and copolymers[1-3]. These novel materials developed through modification of commercially available homopolymers have diverse properties and applications. An extensive use of modified polymers is as hydrogels.

Hydrogels are three dimensional, hydrophilic, polymeric networks capable of imbibing large amount of water or biological fluid. The three-dimensional polymer matrices are characterized by physical crosslinks (entanglements, crystallites) or chemical

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cross-linking (tie-points, junctions). The networks are composed of homopolymers or copolymers, and are insoluble due to the presence of cross links[4,5]. Hydrogels resemble natural living tissue more than any other class of synthetic biomaterials due to their high water contents and soft consistency which is similar to natural tissue. They are termed hydrogels or aquagels[6] when the amount of water retained is between 20-100% of the total weight, and when water content exceeds 100%, these hydrogels are called super adsorbent hydrogels. The chemical structures of the polymer affect the swelling ratio of the hydrogels. Hydrogels containing hydrophilic group swell to a higher degree compared to those containing hydrophobic groups. Hydrophobic groups collapse in the presence of water, thus minimizing their exposure to water molecules. As a result, the hydrogel containing hydrophobic groups, will swell much less compared to hydrogels containing hydrophilic groups. The crosslinks in the polymeric networks make the hydrogels non-soluble in water even at high temperature.

Hydrogels have found a wide range of biomedical applications[7] in the past two decades. Biodegradable polymeric hydrogels are the youngest members of the materials family. An escalation in the contribution of biodegradable polymers towards applications in pharmaceutical, medical and biomedical engineering cannot be overlooked. Biodegradable hydrogels are not limited to release of drugs, peptides or proteins at the characteristic rates and specific site target, but are also extended to medical devices[8] and wound dressing[9], as well as for fabricating scaffold in tissue engineering[10,11]. The success of hydrogels as biomaterials lies in their resemblance to living tissue because of their relatively high water content which minimizes the frictional discomfort by surrounding tissue. The relatively high water content of hydrogels makes them permeable to small molecules like oxygen, nutrients and metabolites. The high solute permeability makes them ideal materials of choice as devices for the controlled release of drugs and other active agents. Much of the research on hydrogels has been focused on the application in controlled drug delivery. An increase in application of hydrogels in the recent past is a matter to reckon with; particularly in the field of biomaterials to replace tissue, organ or function of the body. The nature of these carriers progressed over the years from ceramics, to natural, to synthetic materials. Factors such as integrity, biocompatibility and flexibility were considered, and lead to the use of hydrophilic three dimensional matrices, viz., hydrogels as carrier materials.

To meet the above mentioned demands biodegradable block copolymers have turned out to be promising materials owing to their ability to manipulate their amphiphilic behaviour, mechanical an physical properties by adjusting the ratio of the constituting blocks or adding new blocks of desired properties.

In the textile industry, different dyestuffs, belonging to different classes, are being used in dyeing naturals and synthetics. The effluent discharge of these aromatic compounds from the dye industries poses a major pollution problem since these residual dyes are potent carcinogens. Amongst these numerous techniques of dye removal, adsorption is a process of choice for the removal of organic compounds from wastewater and so a useful tool for protecting the environment[12]. Adsorption of some cationic dyes[13] have been investigated. It could be a viable technique for the safe disposal of textile wastewater into the water streams[14].

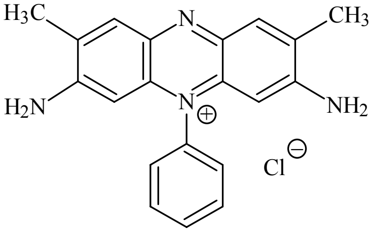
EXPERIMENTAL

Chemicals and materials

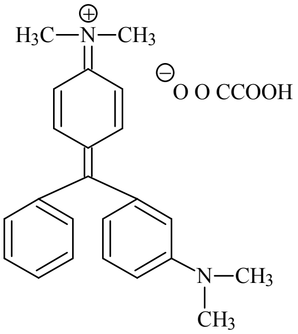
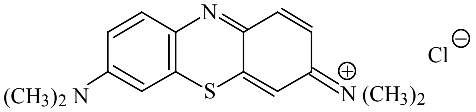
Natural crumb rubber (ISNR – 3L) supplied by Rubber Research Institute of India, Kottayam, Kerala was used for making all the natural rubber (NR) derivatives in the present study. Hydrogen peroxide (30% w/v, E-Merck, India) was used without purification. Toluene (E-Merck, India) was used as solvent without further purification. Toluene diisocyante (TDI) (80/20 mixture of 2, 4 and 2, 6 isomers, Aldrich) was used as received.

Polyethylene oxide or polyethylene glycol of molecular weights (Mn) PEO 8000 (Acros Organics, USA) was used as received. Safranine – T dye (National Chemicals, India) was recrystallised twice from ethanol - water medium. Malachite green and methylene blue (E.Merck, India) were used as such without further purification. The chemical formulae and properties of the dyes are given in Table 1. However the PEO was dried in vacuum oven below their melting point before using them in the synthesis of NR – PEO block copolymer. The chemical formulae and properties of the dyes are given in Table 1.

Table 1: Chemical formulae and some properties of dyes

Name	Chemical formula	Colour index (CI)	Molar mass ($gmol^{-1}$)	λ_{max} (nm)
Safranine T		50240	350.85	520

Cont…

Name	Chemical formula	Colour index (CI)	Molar mass ($gmol^{-1}$)	λ_{max} (nm)
Malachite green		42000	419.51	617
Methylene blue		52015	374	661

Dibutyl tin dilaurate (DBTDL, Merck, India) was used as catalyst without further purification. Chloroform (Qualigens, India, synthetic grade) was used as such. Methanol supplied by Qualigens, India was used as such. Double distilled water was used for cationic dye solution preparation in the swelling and adsorption studies. Absorption spectra were recorded on a Shimadzu V-2450 UV–visible spectrophotometer with matched pairs of silica cuvettes (path length, 1 cm) at a temperature of 308 K.

Synthesis

Preparation of hydroxylated natural rubber or liquid natural rubber (LNR).

The less vigorous but efficient method developed by Ravindran et al.[15] to generate hydroxyl terminated natural rubber (HTNR) using H_2O_2 and solar radiation was adopted.

Natural crumb rubber was masticated for 30 minutes, 400 g of it was dissolved in 4 Ltoluene and solution charged into a 5 L flat bottomed flask of borosilicate glass. Hydrogen peroxide (400 mL) aqueous solution was added and thoroughly mixed with the rubber solution. The mixture was homogenized to a certain extent by addition of 600 mL methanol. The whole assembly with the material for irradiation was placed in sunlight under stirring. After an exposure of seventy hours a layer of water separated at the bottom with some white deposits as byproducts. The upper clear layer comprising liquid rubber in toluene was decanted, distilled to remove the toluene and recovered the HTNR.

The sample for block copolymerisation was purified by repeated precipitation by methanol from toluene solution and dried in vacuum oven. The number average molecular weight (Mn) of HTNR was determined by GPC to be 4700.

Synthesis of NR/ PEO block copolymer

The synthesis was based on a reported procedure[16]. Overall composition of the reactants are given in Table 2.

Table 2: Overall compositions of the block copolymers

Sample	Molar composition	Wt. % of PEO	Wt. % of NR
NR : PEO 8000	1 : 2.1 : 1	62.91	37.09

HTNR dissolved in chloroform (23% w/v) dibutyl tin dilaurate catalyst (0.3 % by wt of HTNR) was added and the solution brought to reflux with stirring. The stoichiometric amount of TDI was added in drops followed by addition of the required amount of PEO as a solution in chloroform (23% w/v) drop wise during a period of 1.5 hrs followed by 2 hrs of the reaction. Excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone releasing agent. The sheet was removed from the tray after 12 hrs kept in a vacuum oven at 600^{o}C to remove the traces of solvent present and then cured at 700^{o}C for 24 hrs, followed by one week ageing at room temperature in a moisture free atmosphere.

Polymer designation

The block copolymer prepared from LNR and PEO-8000 is denoted as BC-4. The dye stained Block copolymer is represented as BC-4.MG, BC-4.ST and BC-4.MB. Samples were prepared and performed the following analysis for consistent data.

Characterization of the samples

UV-Visible Spectral Analysis of virgin & dye stained NR/PEO block copolymers.

Discs of radius of 1.5 cm of each of the BC in the series were left to swell in the aqueous solution of MG, ST and MB (2.478 x 10-5 moles/litre) to reach equilibrium swelling. These were then lifted out of the solution dried at room temperature and left in desiccator for two days. The solid state spectra of these dried samples were recorded.

The dyes, solid virgin block copolymer (BC-4), the dye stained BCs (BC-4.MB, BC-4.ST and BC-4.MG) were characterized by UV-Visible solid state spectroscopy on a

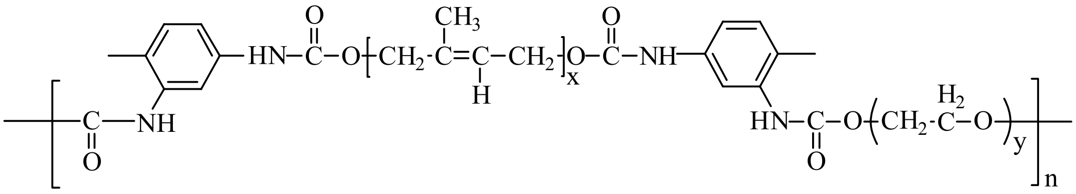
Shimadzu V-2450 UV–visible spectrophotometer using a diffusive reflectance spectral attachment at a temperature of 289 K. The baseline was recorded by placing a sample holder with barium sulphate & another with a reference in and running the spectrum from 200 nm to 800 nm. Then the barium sulphate was replaced with a sample holder with solid disc of solid virgin block copolymer (BC-4) or the dye stained BCs (BC-4.MB, BC-4.ST and BC-4.MG), which were held in place in the sample holder with the help of a double sided sticker and the solid state spectrum was recorded in the absorbance mode. The spectra of the dyes (as solid powder) were taken by pressing the powdered dye into the circular depression in the sample holder, replacing the sample holder with barium sulphate & recording the solid state spectra. X-ray diffraction analysis of virgin & dye stained NR/PEO block copolymers.

Circular disc BC-4 was taken and besides three discs of BC-4 was loaded with the different dyes, viz., MG, ST and MB by swelling to equilibrium state in the three acqueous dye solution of 2.5 x 10-5 mol/L strength and subsequently drying in the vacuum oven. The circular discs of the virgin and three dye doped block copolymers (BC) of BC-4 were subjected to X ray diffraction studies on a Bruker D8 Advance X-ray diffractometer using CuKα X rays.

RESULTS AND DISCUSSION

Synthesis

Following the above procedure, sheets of a series of polyether-diene block copolymers were prepared. The polyether is the PEO part and the polydiene is liquid natural rubber (LNR), which provides the nonpolar part. The block copolymers were prepared by solution polymerisation method and their structure is represented in **Scheme 1**. The sheets of the five block copolymer was honey coloured and on curing and ageing BC-4 was developed into firm sheets (plastic) whereas BC-1 and BC-2 acquired a more flexible nature (elastomeric).



Scheme 1

Characterization of the virgin and dye stained block copolymer

UV-Visible spectral analysis

The UV-Visible spectra of MG (Fig. 1) reports absorption maxima centered at 617 and 424 nm, which can be ascribed to the S0-S1 and S0-S2 transitions of π-π* transition, respectively[16]. However the solid state UV-Visible spectra of MG shows a broad band at 702 nm (abs 1.492) and 473 nm (abs 1.526) assigned to the π-π* transition. This is shown in Fig. 1 which depicts the UV Visible solid state spectra of (a) MG (b) BC-4 and (c) the MG stained BC-4. The spectrum of BC-4 does not show any peak in the visible region. However in BC-4.MG, a band at 629 nm (abs 1.27) is observed (Table 3). This could be considered to be a hypsochromic shift of 73 nm of the π-π* transition band at 702 nm of MG. A corresponding shift of the band at 473 of MG in BC-4.MG is however not observed. The above mentioned shift, which implies dye uptake, can be accounted for in the following manner.

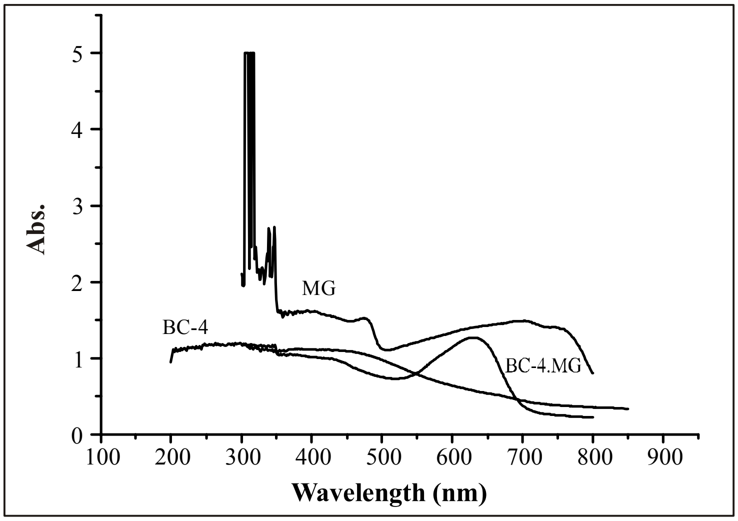


Fig 1: UV-Visible spectra of MG, BC-4.MG and BC-4

Discs of radius of 1.5 cm of each of the BC in the series were left to swell in the aqueous solution of MG, ST and MB (2.478 x 10^{-5} moles/litre) to reach equilibrium swelling. These were then lifted out of the solution dried at room temperature and left in dessicator for two days. The solid state spectra of these dried samples were recorded. During swelling the acquated MG molecules and water diffuse into the matrices of the block copolymer. The hydrophobic isoprene segments shrink and the hydrophilic PEO segments relax in water causing the mesh size to increase. This facilitates diffusion of the dye molecules into the PEO domains, wherein they may be bound or unbound to the ethereal oxygen[17]. On drying the BCs that have absorbed the dyes, the swollen gel retracts maintaining the disc shape, whereby the mesh size decreases causing the MG molecules (the bound and unbound dye) to come closer and aggregate. This leads to π-π stacking and intermolecular repulsion of the dye molecules, which in turn leads to raising of the LUMO (π*) HOMO (π) and of the dye molecules; thus the excitation energy increases for π-π*increases in BC-4.MG and thus a hypsochromic shift on complexation of the block copolymer with cationic dyes occurs.

Table 3: Absorption maxima of virgin and dye stained BC-4 copolymers in MG, ST and MB

Sample	Band position (nm)	Absorbance	Hypsochromic shift (Δλ)
MG	702	1.492	
BC-4.MG	629	1.270	73
ST	548	1.44	
BC-4.ST	435	1.20	98
MB	741	1.30	
BC-4.MB	650	1.18	91

Hypsochromic shift is observed in BC-4.ST and BC-4. MB of the order of 109 and 86 nm, respectively could be explained as above. The ST and MB molecules also undergoes aggregation in the above two samples respectively, which accounts for the hypsochromic shifts of BC-4.ST and BC-4.MB.

X-ray diffraction analysis

Fig. 2 depicts the XRD of BC-4, BC-4.MG, BC-4.ST and BC-4.MB. BC-4 shows peaks at 2θ 35.79 (d = 2.507 and intensity count 4812). The appreciable intensity of the peak of BC-4 suggests that it is fairly crystalline.

Results of X-ray diffraction of the NR/PEO block copolymer before and after the absorption by different dyes are shown in Table 4.

This technique is used to represent the morphological structure and the changes in its crystal form resulting from the effect of swelling and interaction of pollutant compounds (dyes) onto the hydrogel polymer structure. The diffraction curves of the dye uptake in the hydrogel record the change between 2θ before and after the dye's uptake is observed.

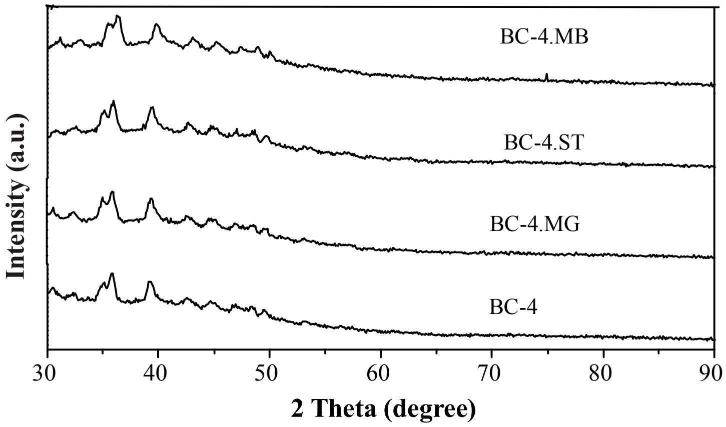


Fig. 2: X-ray diffraction patterns of the virgin and three dye doped BC-4 block copolymers

The integrated intensity (counts) is taken as an indication of the amorphous and crystallinity percentage of the polymer according to the area under the peak obtained from the X-ray diffraction patterns. It is shown in the Table 4 that the hydrogel-dye free and hydrogel-dye complexes are in the crystalline state and although an increase in intensity is observed on dye complexation, it is not of much significance (a difference in intensity of the order of thousands would be required to claim enhancement in crystallinity). Regarding the d values, it is observed that there is not much variation in its values in BC-4 and the corresponding dye stained BC-4.MG, BC-4.ST and BC-4.MB.On interacting with the MG, ST and MB the BC-4 block copolymer shows an increase in 2θ, viz., from 35.79 to 35.89, 35.89 and 36.41 for BC-4.MG, BC-4.ST and BC-4.MB. But this also is not of much significance. Hence it can be surmised that cationic dye complexation does bring about significant changes in the crystallinity of the block copolymers. Hence change in the firmness of this plastic material is not observed.

Table 4: X-ray crystalline data of virgin and dye stained block-copolymer (BC4)

Lattice parameters	BC-4	BC4.MG	BC4.ST	BC4.MB
2θ	35.79	35.89	35.89	36.41
d (nm)	2.50	2.499	2.499	2.465
Integrated intensity	4812	5250	4623	5090

The above result is favorable since the lack of change in the firmness of the sheet, makes the dye stained BC-4 usable as hydrogels in controlled dye/drug delivery. Some of the cationic dyes are known to be used as antiseptic (Crystal violet) and anticancer drugs. It is essential that the swollen drug-loaded hydrogels be soft and pliable like the body tissues to prevent friction and make the material biocompatible.

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