An Aqueous Process to Graft 2-Hydroxyl ethyl Methacrylate onto Polyvinyl Chloride Through Its Functional Group

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ABSTRACT: A simple aqueous method has been discussed to graft 2-hydroxyl ethyl methacrylate (HEMA) onto the surface of polyvinyl chloride through its functional group (—OH). This method involves the conversion of the —OH group of HEMA to —ONa using metallic sodium. The modified surface has been characterized using FT ATR-IR and Scanning electron microscopic methods. The advantage of the method is the feasibility of using the intact double bond of HEMA for further reaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 113–118, 1999

Key words: PVC; HEMA; FT ATR-IR

INTRODUCTION

The properties of a surface can dramatically be altered by the adsorption or grafting of polymeric entities. A coating or grafting of a polymer on a relatively inert surface, for example, can enhance the adsorption of an additional layer of other entities such as proteins. In fact, surface modification has been followed extensively to improve the properties of the substrates like enhanced adhesion, improved blood compatibility, etc.¹ The approach of surface modification is perhaps the simplest route to tailor the commercially available synthetic polymers for blood-contacting applications.

Polyvinyl chloride (PVC) is one of the largely consumed polymers in terms of its commercial applications. This polymer also finds wide uses in the medical field, mainly as containers for blood, blood products, IV fluids, etc.² A serious drawback of this polymer is the reduced compatibility within a biological environment. Efforts to improve its blood or tissue-contacting properties have been attempted largely by surface modification through grafting of different entities.^{3,4} This processes, though specifically intended for the modification of surface alone, often takes place in the bulk phase, leading to an alteration in the properties.

The coupling of the monomer preferably to the surface alone through their functional groups (e.g., the —OH groups) and further polymerization by free radical initiation appears to be an interesting possibility to improve the surface with additional entities. For example, grafting of HEMA through the —OH group to PVC surfaces and the further polymerization of the grafted monomer would be an interesting procedure for modifying the surface. This approach, as far as we know, has not been reported. This communication describes a simple approach of using Williamson synthesis⁵ to attach HEMA through the —OH group onto the surface of PVC.

EXPERIMENTAL

Commercial PVC containing nearly 32% Di 2-ethyl hexyl phthalate as a plasticizer and a

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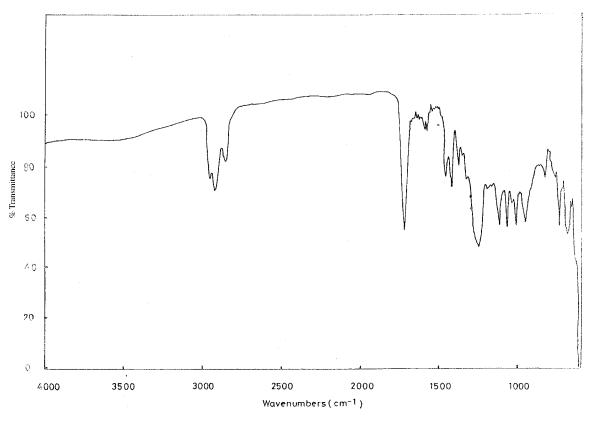


Figure 1 FT-ATR-IR spectrum of PVC.

weight-average molecular weight of 62,000, was used for the studies. PVC films without the additives were also used for the modification. HEMA obtained from Sigma Chemicals, St. Louis, MO, was used after purification by vacuum distillation. All other analytical grade chemicals were obtained from Spectro Chem, Bombay, India.

In Williamson's reaction, the —OH groups react with metallic sodium to form —ONa, as shown below.

$$2 \text{ R}$$
—OH + $2 \text{ Na} \rightarrow 2 \text{ R}$ —ONa + H₂

where R is an alkyl group.

A calculated amount of metallic sodium was allowed to react with HEMA at room temperature $(30^{\circ}C)$ overnight. The reaction scheme is shown below.

$$2 \text{ H}_2\text{C} = \text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2 - \text{OH} + \text{Na} \rightarrow$$
$$2 \text{ H}_2\text{C} = \text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{ONa} + \text{H}_2$$

PVC strips were directly placed in the solution for 30-40 min at 60-70 °C. The PVC strips were

then washed with water and dried in a vacuum oven at 40°C. The replacement of the H atoms by sodium in the final product was confirmed by flame photometry.

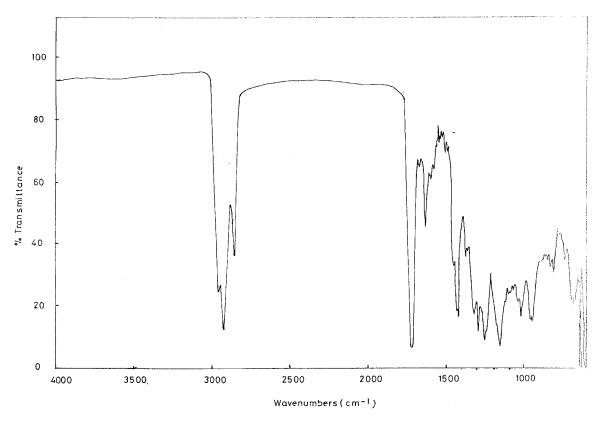
A Nicolet Inc. model Impact 410 FT infrared spectrophotometer and a horizontal ATR accessory (Nicolet Inc, USA) were used to obtain the ATR spectra of the polymers. The number of scans was 50.

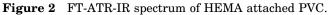
An Hitachi model S-2400 scanning electron microscope was used for obtaining the surface features of the polymers. A thin layer of gold was coated prior to the observation. The stress–strain parameters were estimated using an Universal testing machine as per ASTM D882 (Instron Co., UK).

Further polymerization of the grafted HEMA was carried out by gamma-irradiation from a ⁶⁰Co source (Panoramic batch irradiator, BARC, Bombay, India).

RESULTS AND DISCUSSION

Figure 1 shows the ATR-IR spectrum of PVC. The spectra show the characteristic features of the





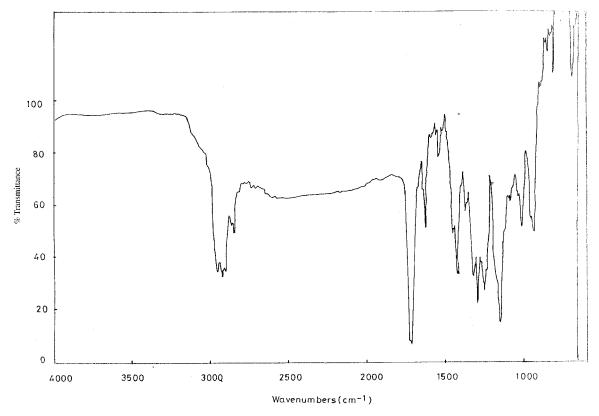
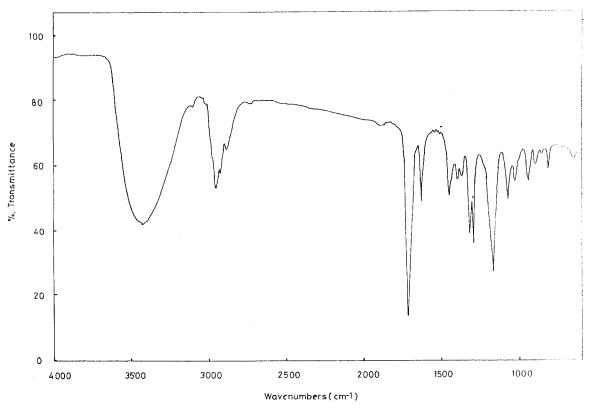
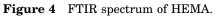
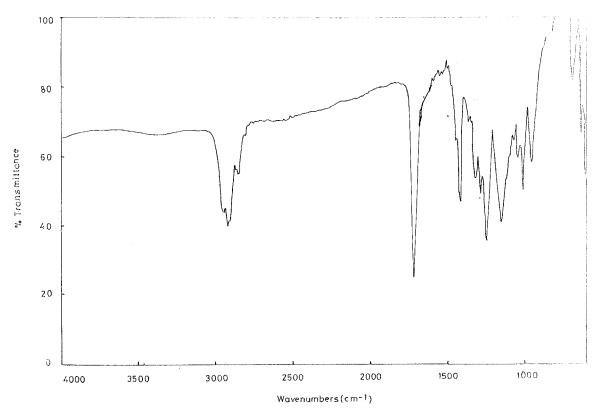


Figure 3 Difference spectrum of PVC-HEMA and PVC.



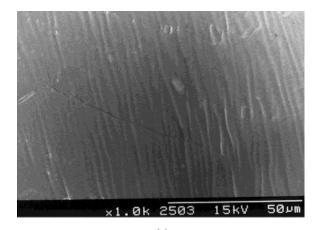




 $\label{eq:Figure 5} {\ \ \ } {\ \ \ } {\ \ } {\ \ } {\ \ \ \ \ } {\ \ } {\ \ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ \ } {\ \ \ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ } {\ \ \ } {\ \ \ \ \ \ \ } {\ \ } {\ \ \ \ \ \ } {\ \ \ \ }$

plasticizer, which constitute nearly 32% of the polymer. Figure 2 illustrates ATR-IR spectrum of HEMA-coupled PVC. The prominent feature of the spectrum comparing to the spectrum shown in Figure 1 is a strong peak associated with ether linkage around 1140 cm^{-1} . The presence of this peak suggests that HEMA is coupled to PVC through the -O- atom. Figure 3 depicts the difference between the spectrum of PVC-HEMA and PVC. The spectrum has almost all features of the transmission spectrum of the HEMA monomer shown in Figure 4. The absence of the --OH group in the spectrum is notable. This is indeed expected, in the sense that, the coupling of HEMA to PVC has taken place through the conversion of the —OH groups to —ONa. The 1630 cm^{-1} peak of C=C of the HEMA monomer is also present in the difference spectrum, indicating that the C=C bond is intact after the coupling reaction.

Figure 5 is the difference spectrum of the PVC-HEMA surface after gamma-irradiation. The no-



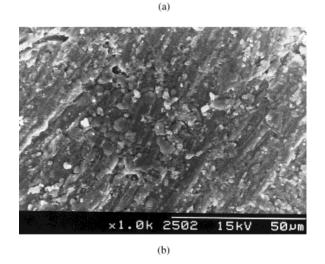


Figure 6 Scanning electron micrographs of (a) control PVC, (b) modified PVC.

Table IStress-Strain Parameters ofthe Polymers

| Polymer | Stress (MPa) | Strain (%) |
|---------------------------------|-----------------------------------|----------------------------|
| PVC (Control) PVC (Modified) | 32.03 ± 2 31.66 ± 1.72 | $576 \pm 16 \\ 566 \pm 21$ |

table change of the spectrum compared to the spectrum of the PVC-HEMA spectrum (Fig. 3) is the absence of the peak at 1630 cm⁻¹ associated with the double bond. The disappearance of this peak suggests that the HEMA monomer is converted into a polymeric form.

Figure 6(a,b) shows the SEM micrographs of PVC and HEMA-grafted PVC. The surface realizes a different morphology as a result of grafting. Unlike the other processes of surface modification, in the present method we feel that the modification is confined to the surface alone. The probability of diffusion of the modified monomer to the bulk of the polymer is a bit less. This conclusion is arrived at based on the lack of any weight increase of the polymer samples kept in the aqueous solution of the modified monomer for a period of 1 week. The mechanical properties of the polymers are summarized in Table I. Hardly any changes are noticed in the stress-strain parameters of the polymers before and after the grafting process. This further indicates that the grafting is confined to the surface. It may be relevant to point out that bulk modification through grafting normally deteriorates the mechanical properties.

Surface modifications of synthetic polymers have been vigorously followed to enhance the range of their applications.⁶⁻⁸ Most of these methodologies are based on the grafting of vinyl monomers by radiation, thermal, or chemical processes. The method described here provides an alternative way of introducing the monomer through their functional groups. The intact double bond could be used for the coupling of other entities through free radical initiation to create a surface containing more than one entity. The advantage of the method is the confinement of the grafted chains mostly to the surface. Though not discussed here, we grafted an additional entity (NVP) onto the HEMA-coupled PVC. This approach may be useful in functionalizing the surface with the desired components to get an optimum balance of hydrophilicity and hydrophobicity. The modification process can also be carried out on PVC resin. After the modification, the resin may be processed further by incorporating other additives.

The immobilization of enzymes onto the surfaces is followed by activation of functional groups for coupling. The chemical reaction may affect the useful life of the immobilized biomolecules. In the present case, the sensitive biomolecules may be adsorbed onto the surface and can subsequently be trapped by free radical polymerization through the intact double bond of the coupled monomer. In such cases, because the functional groups of the biomolecule are not involved in the reaction, the effectiveness of the system may be prolonged. Using this new route, these possibilities could be explored.

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