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BLENDS EPOXiDIZED OIL/ACACIA POLYMERIC FILMS AND THEIR EFFECT OF EXTERNAL STIMULI ON THE EQUILIBRIUM SWELLING PROPERTIES

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ABSTRACT

Polymeric films were developed from the epoxidized oil with different ratios of polyamide and Gum *acacia* blending. The influences of external stimuli such as pH, temperature and ionic strength of the swelling media and the type of buffer on the equilibrium swelling properties were investigated. Equilibrium and oscillatory swelling studies were also performed to investigate the film response to changes in the pH of the swelling medium. Polymeric films showed typical pH and temperature response such as low-pH and low-temperature have maximum swelling while high-pH and high-temperature show almost complete deswelling. Moreover, it was attributed that the polymeric films/hydrogels with higher concentration of epoxidized oil and Gum *acacia* showed higher rate of swelling while the films with high amount of DGEBA epoxy and low concentration of epoxidized oil have minimum possible swelling.

Key words:: DGEBA epoxy, epoxidized oil, polymeric films, swelling, blends

INTRODUCTION

When a polymeric network is immersed in an appropriate solvent, it swells. The hydration power or water absorption is one of the most important factors, which determined by the functionality and quality of the'hydrogel, moreover the majority of the properties are directly influenced by this one. The behaviour of highly swollen hydrogels is therefore a function of the network characteristics[1].

Crosslinked polymers containing DGEBA epoxy and their blend can be prepared and modified for various applications in the field of controlled release[2]. For example, it is possible to develop pH-sensitive hydrogels that response to the physiological environment[34]. More specifically, anionic gels could be utilized for controlled release of drugs in alkaline environments whereas cationic gels could release in acidic environments[48]. Some of the more important biomedical applications in which hydrogels with pH sensitivity could be used include artificial muscles, components in chemical separation systems, controlled drug delivery devices, site-specific gastrointestinal delivery devices, and buccal, or nasal controlled release systems[211].

Hydrogels have been used widely as biomaterials because the high water

content renders them biocompatible to the body tissues[1214]. As a result, hydrogels have also been investigated intensively over the last decade for use in controlled drug release systems and a variety of other biomedical purposes such as medical implants, diagnostics, bioreactors, and bioseperators[1215]. Hydrogels are of particular interest in drug delivery applications because their internal architecture can be manipulated to dimensions that accommodate the molecular sizes of the peptide and protein drugs. In addition, the content, density, and length of the crosslinking groups can be used to regulate the pore or mesh size of the swollen hydrogel through which the entrapped drug traverses and is released. As a consequence, hydrogels can be prepared to possess tailored 6internal structures that provide specific release rates for different drugs. Alternatively, the hydrogel matrix can also be manipulated to specifically retain drugs within the crosslinked network. In this case, drug release can be restricted until degradation of the hydrogel matrix takes place. The weight ratio of swollen polymer to the dry polymer (g swollen polymer/g dry polymer) is called the swelling ratio, q.The ratio of the volume of the swollen polymer to the volume of the dry polymer is termed the volume degree of swelling.

In the present work, novel blends polymeric hydrogels of epoxy-polyarrude/ *acacia* were investigated for their equilibrium swelling properties to the different physiological environments.

EXPERIMENTAL

Material and methods

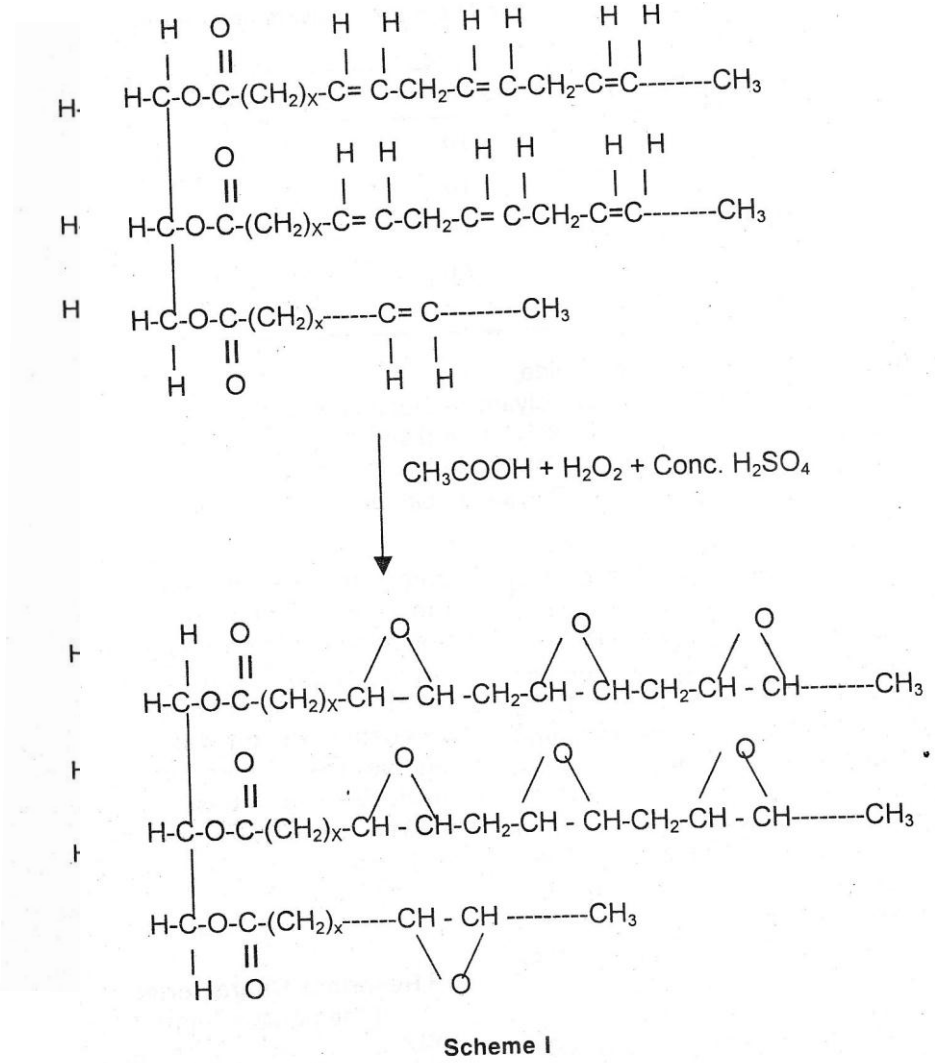
NaH_2P0_4, K_2HP0_4, and H_3P0_4 used to prepare phosphate buffer and tri-sodium citrate, sodium dihydrogen citrate and citric acid of AR grade procured from SRL, India were used to prepare citrate buffer. DGEBA (diglycedyl ether of bis-pheno! A) epoxy (epoxy equivalent wt. = 180), and polyamide (amine no. 35) were purchased from Shankar Dyes and Chemicals, Delhi. Gum *acacia* was purchased from s.d fine Chemical Ltd. Oil was extracted from linseed (obtained from local market) through soxhlet apparatus. Petroleum ether (b.p. 60-800 ° C) was used as solvent. Hydrogen peroxide (30%), glacial acetic acid, sulphuric acid, diethyl ether, and benzene used were of analytical grade.

Epoxidation of Oil

Epoxidized oil from linseed oil was prepared using the reported method for the synthesis of vegetable oil epoxy[16]. Linseed oil 40 g (Iodine value = 180) equivalent to 0.2899 mol of unsaturation, 40 mL of benzene. 7.995 mL (0.1326 mol) of glacial acetic acid, and one mL of concentrated sulphuric acid diluted to 50% with water were taken in a three necked round bottom flask equipped with mechanical stirrer, dropping funnel and thermometer. The flask was then immersed in cold water bath; 48.5 mL (0.427 mol) of 30% hydrogen peroxide was added drop wise with continuous stirring. The temperature of the reaction mixture was kept below 20°C during the addition of entire hydrogen peroxide. The temperature was then raised to 60°C which was maintained till the reaction continued. The progress of the reaction was monitored by determining the epoxy equivalent[17] at regular intervals. The reaction progress is shown in **scheme I.**

Free Standing Polymeric Films

Four components were used in the preparation of epoxy-polyamide/Gum *acacia* blended hydrogels, namely epoxidized oil, DGEBA (epoxy equivalent = 180) epoxy, polyamide (amine number = 35),and Gum acacia powder. Epoxidized oil prepared as above was blended with DGEBA epoxy in a reaction vessel under vigorous stirring at 65°C. Polyamide was added (as a crosslinker) slowly to the



Scheme I

blended epoxy at 45°C and stirring was continued for another 4-5 minutes til) it completely mixed and cured. The cured epoxy-polyamide systems were further blended with different ratios of Gum acacia at room temperature as shown in Table 1. Blending was done with stirring and pressing process. The blended polymers were poured onto the glass straws of known diameter. When the sample was almost dried, it was placed on a vacuum line to remove the last traces of solvent. The copolymer/hydrogels developed in a long cylindrical shape glass straw were cut into pieces of 1-3 mm in thickness and were used for the swelling deswelling studies.

Equilibrium swelling studies

Dried epoxy-polyamide/Gum acacia blended films (3-4 mm thickness, 8-10 mm diameter) were left to swell in a solution of desired pH (2.5 - 9.0), ionic strength

Table -1: Compositions of the five epoxy-polyamide/Gum *acacia*

Samples	ECTO	DGEBA	Polyamide	Acacia
EP	10g	10g	10g	-
EP-b-A06	10 g	10 g	10 g	70 g
EP-b-A03	lOg	lOg	lOg	16g
EP-b-A05	7.0 g	7.0 g	• 7.0 g	21 g
EP-b-A10	15 g	5.0 g	5.0 g	10.7g

Note: EP = Epoxy-Polyamide
EP-b-A06 = Epoxy-polyamide blend Acaci (30:70)
EP-b-A03 = Epoxy-Polyamide blend Acacia (65:35)
EP-b-A05 = Epoxy-Polyamide blend Acacia (50:50)
EP-b-A10 = Epoxy-Polyamide blend Acacia (70:30)

(/ = 0.2 M), and temperature 35°C. The films were weighed before and after contact with aqueous solutions. Swollen films were removed from the bath at regular intervals, were quickly and carefully dried superficially with filter paper weighed and placed in the same bath. Measurements were continued until a constant weight was reached for each sample. The equilibrium weight of swelling percent *(EWS* %), of the polymer was calculated. Measurements were performed in triplicate.

The percentage equilibrium weight of swelling can be expressed as[20]:

$$EWS\% = [(W_{wet(}-W_{dry})/W_{dry}]x100$$

where, W **wet** is the weight of the wet sample at time t and W_{dry} is the weight of the dry sample.

Oscillatory Swelling Behaviour

. The swelling-deswelling behaviour of epoxidized oil/Gum acacia blended polymeric films was monitored by placing the samples into acidic solution of pH 3.0 to swell, allowed to deswell in basic solutions of pH 8.0 repeatedly. Each samples were placed in the external solution of pH 3 and allowed to swell completely, it was monitored carefully by the removal of swollen films from the solution and dried superficially with filter paper weighed and placed in the same bath. Measurements were continued until a constant weight was reached for each sample. The same process was repeated for deswelling in basic solutions of pH 8. Measurements were performed in triplicate.

RESULTS AND DISCUSSION

pH Response Characteristics

If the polymer matrix contains some ionizable groups, which can dissociate or get protonated at some suitable pH values of the external medium, then the swelling capacity of the hydrogel is affected by the variation in pH. In the present study, the effect of the pH of the swelling media on the swelling behavior of the four epoxy-polyamide/acacia blend hydrogel samples (Table 2) has been studied in the pH range 2.5 - 9.0. It is clear from the Figure 1 that the sample EP does not show any change in the equilibrium weight swelling with the pH of external medium, whereas for the samples EP-b-A06 & EP-b-A10, which contain Gum *acacia,* the equilibrium water

Table- 2: The % EWS values of acacia blended epoxy-polyamide systems in phosphate and citrate buffer solutions at 35°C

System	Phosphate buffer		Citrate buffer	
Samples	**ECTO**	**DGEBA**	**Polyamide**	**Acacia**
EP	10g	10g	10g	-
EP-b-A06	10 g	10 g	10 g	70 g
EP-b-A03	lOg	lOg	lOg	16g
EP-b-A05	7.0 g	7.0 g	• 7.0 g	21 g
EP-b-A10	15 g	5.0 g	5.0 g	10.7g

Table -1: Corr	Ionic strength 0.01 M	Ionic strength 0.10 M	Ionic strength 0.20 M	Ionic strength 0.01 M	Ionic strength 0.10M	Ionic st 0.20 M
pH 3						
EP	6.35	6.22	6.21	5.95	5.90	5.40
EP-b-A06	30.21	26.15	24.20	30.00	25.88	22.62
EP-b-A03	20.36	17.52	12.80	18.75	15.96	14.12
EP-b-A05	23.92	18.39	13.81	21.43	17.92	12.43
EP-b-A10	27.86	24.16	21.15	25.81	22.70	18.63
pH 8						

uptake decreases as the pH increased in the range 2.5 - 9.0. The pH-independent swelling behavior of sample EP may be attributed to the fact that since the polymer matrix is highly cross-linked therefore, variation in the pH of the external media does not change in the swelling capacity. However, the situation is quite different with the samples which contained Gum *acacia.* It is much more pronounced near the pH 3.0 and 4.0, which may be attributed to collapse the crosslinked chains of the polymers around this pH values. Therefore, when the pH of the external medium at pH 4.0 or below, the volume collapse of the gel matrix causes a sudden increase in swelling due to increased in ion osmotic swelling pressure, as well as chain relaxation resulting from the electrostatic repulsion among the macromolecular chain.

Experiment results of the pH dependence on the equilibrium weight swelling of Gum *acacia* blended epoxy-polyamide systems are shown in Figure 1. The abrupt decrease in swelling was observed in the acidic pH region and continued through pH = 9. A very steep decrease in pH dependence was exhibited between pH = 7.4 and pH = 9. In general, the equilibrium swellings were greater for the films containing increasing amount of Gum *acacia* and epoxidized oil. However, the films with higher concentration of DGEBA epoxy showed minimum possible swelling. The equilibrium weight swellings were a function of the amount of epoxidized oil and Gum *acacia.*

The epoxy-polyamide (EP) cured system showed very negligible swelling ratios due to highly cross-linked polymeric chain between amine of polyamide and

oxirane groups.

Thus in all the cases, equilibrium weight of swelling is very much low in basic medium and as we decrease the pH value we get a higher percent of weight swelling. To sum up, the observed decrease in equilibrium water uptake with rise jn pH of the external medium causes an increase not only in the ion osmotic swelling pressure, but also in the extent of the chain relaxation process.

Ionic Strength-Responsive Characteristics

The effect of external ionic strength on the equilibrium weight of swelling of epoxy-polyamide/acacia blends polymeric films at 35°C is given in Fig. 2 (a) & (b). pH of the solution was fixed at 3.0 and 8.0 to obtain minimum and maximum swelling for each polymeric film/gel, as the effect of ionic strength is clearly observed at these two pH. It is observed in Fig. 2 that with increasing ionic strength of the solution the equilibrium weight swelling values show a continuous decrease and this effect becomes more pronounced at pH 3 than at pH 8. An increase in the ionic strength generally caused a decreased in the swelling, as the difference in concentration of mobile ions between the gel and solution is reduced causing a decrease in the osmotic swelling pressure of these mobile ions inside the gel[16].

The effect of relative amounts of *acacia* in the polymeric film/hydrogel system can be clearly seen by comparing the ionic strength dependence of the equilibrium weight swelling of EP-b-A06 and EP-b-A10.The changes of equilibrium weight swelling were observed most clearly at the fully swollen state (pH 3.0). When the ionic strength of the medium was increased from 0.01 to 0.20 M the equilibrium weight swelling was observed to decrease by 6 wt.% at pH 3 and pH 8 for EP-b-A06 and EP-b-SA10 respectively. In the case of EP-b-A03 the *EWS* was observed to decrease by 8 wt.% and 4 wt. % at pH 3 and 8 respectively. About 10 wt.% and 6 wt.% decrease in weight swelling was observed at pH 3 and 8 respectively in EP-b-A05 system. The epoxy-polyamide (EP) cured systems without starch shows a negligible weight swelling changes to all concentrations and at both pH levels.

Temperature Responsive Characteristics

Figure 3 (a) & (b) represent the influence of the temperature on the equilibrium degree of swelling of *EP/acacia* blend hydrogels in phosphate buffer solution at pH 3 and pH 8 respectively. The equilibrium degree of swelling of epoxy-polyamide (EP) cured system in pH 3 and pH 8 phosphate buffers is also discussed. Figures show that the epoxy-polyamide/ acacia blend hydrogels exhibit large continuous changes in the swelling behavior of the films as a function of temperature. These changes attributed are presumably due to the rupturing of structure of the hydrogels upon warming. It has been shown that a number of hydrogels demonstrate nearly continuous volume transition and associated with the phase transition from a low temperature, highly swollen gel network collapsed at high temperature phase near their critical points[1819]. The phase transition is analogous though fundamentally distinct from the lower critical solution phase transition (LCST).Thus the polymeric films rich in starch or higher epoxidized oil can be expected to exhibit volume collapse upon warming.

However, due to the slight decrease of equilibrium weight of swelling of EP (epoxy-polyamide) cured systems a sharp volume transition was not observed at both pH values in the temperature range of 4-65°C (Fig. 3 (a) & (b)). The degrees of weight swelling of epoxy-polyamide cured systems are 6.26 and 5.14 at 0°C in the pH 3 and pH 8 buffer solutions respectively.

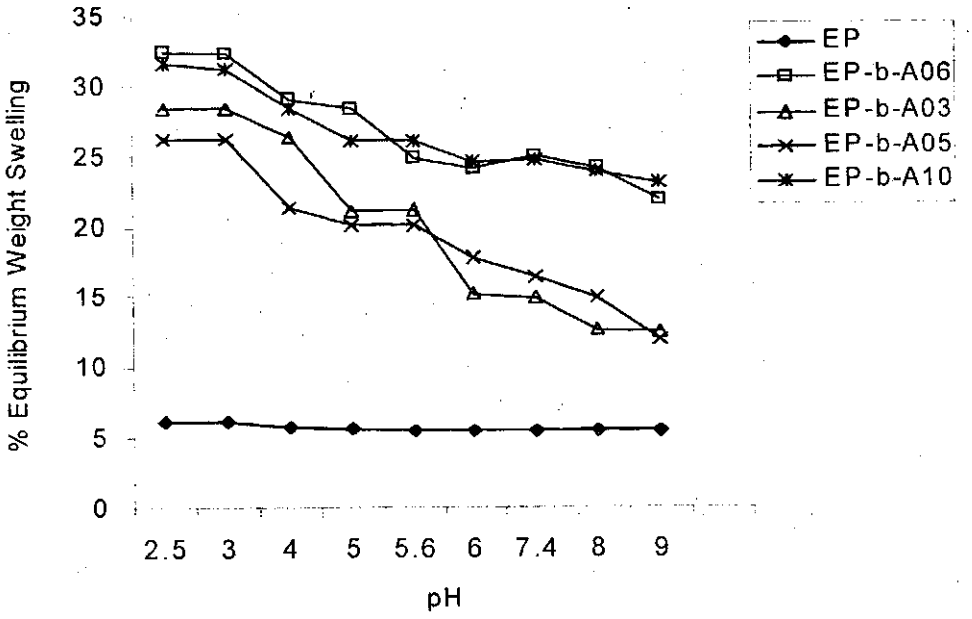


Figure 1 - Effect of pH on the equilibrium weight of swelling value of epoxy-polyamide/acacia blends polymeric films

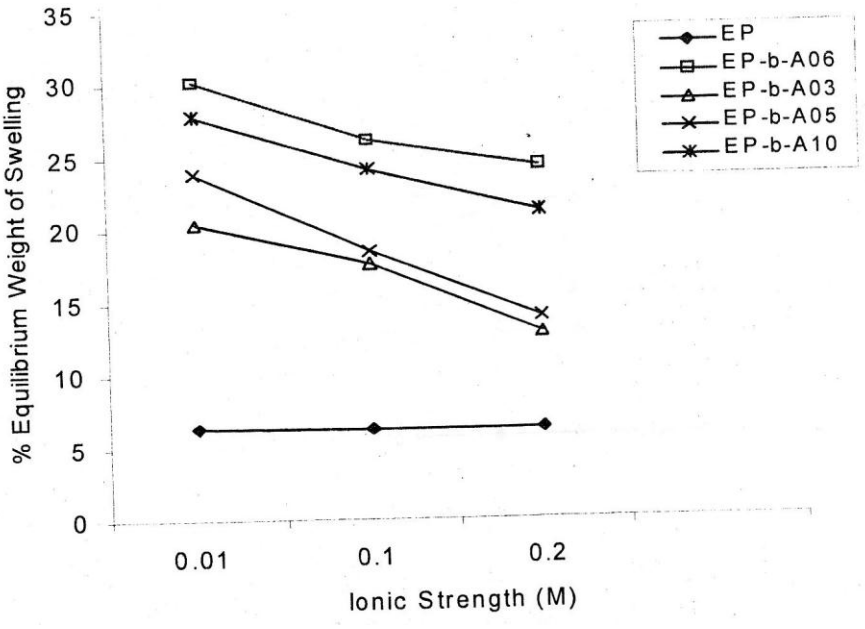


Figure 2 (a) - Effect of ionic strength on the equilibrium weight of swelling values of epoxy-polyamide/acacia blends polymeric films at pH 3

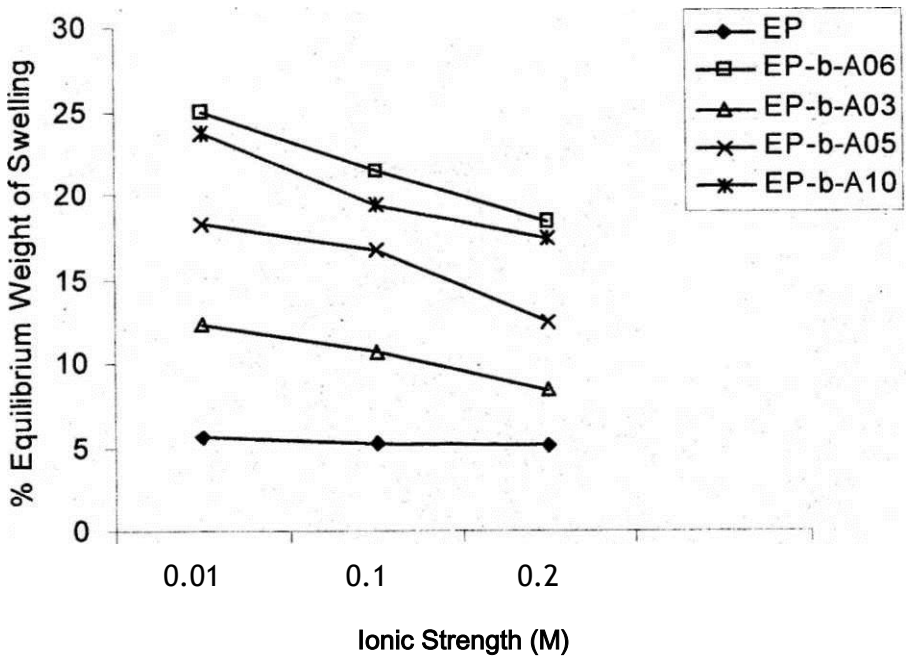


Figure 2 (b) -Effect of ionic strength on the equilibrium weight of swelling values of epoxy polyamide/acacia blends polymeric films at pH 8

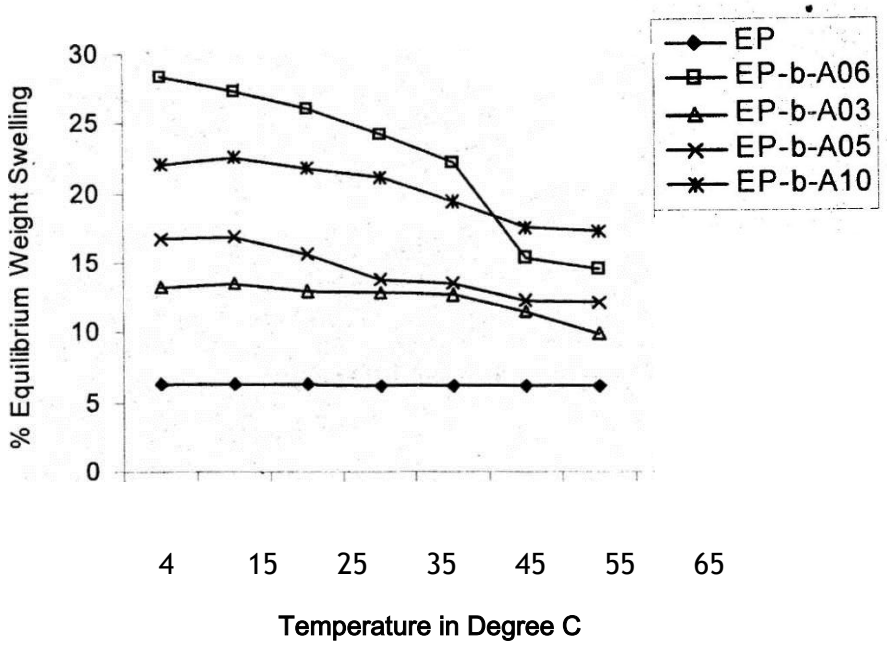


Figure 3 (a) -Effect of temperature on the equilibrium weight of swelling of epoxy' polyamide/acacia blends polymeric films at pH 3

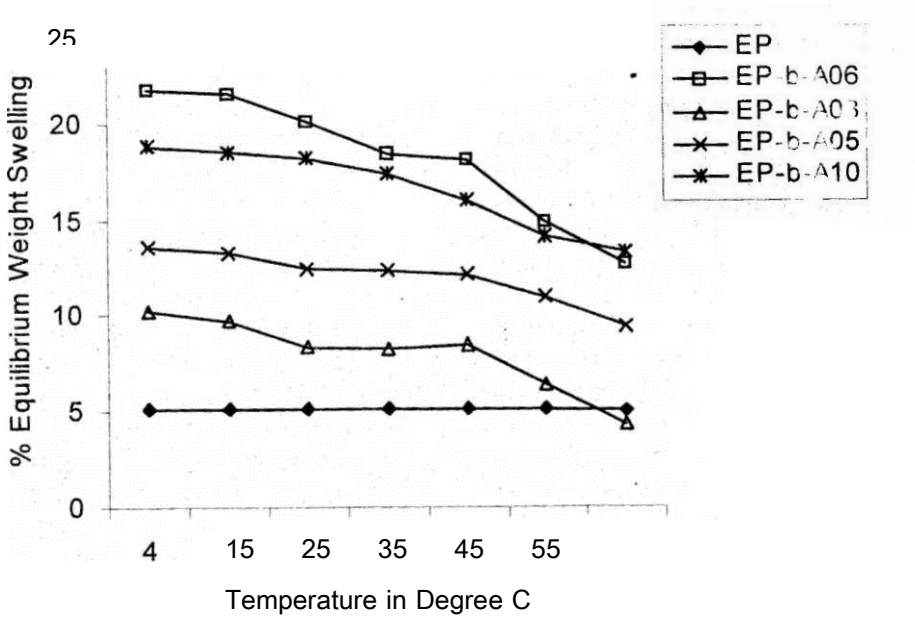


Figure- 3 (b) -Effect of temperature on the equilibrium weight of swelling of epoxy-polyamide/acacia blends polymeric films at pH 8.

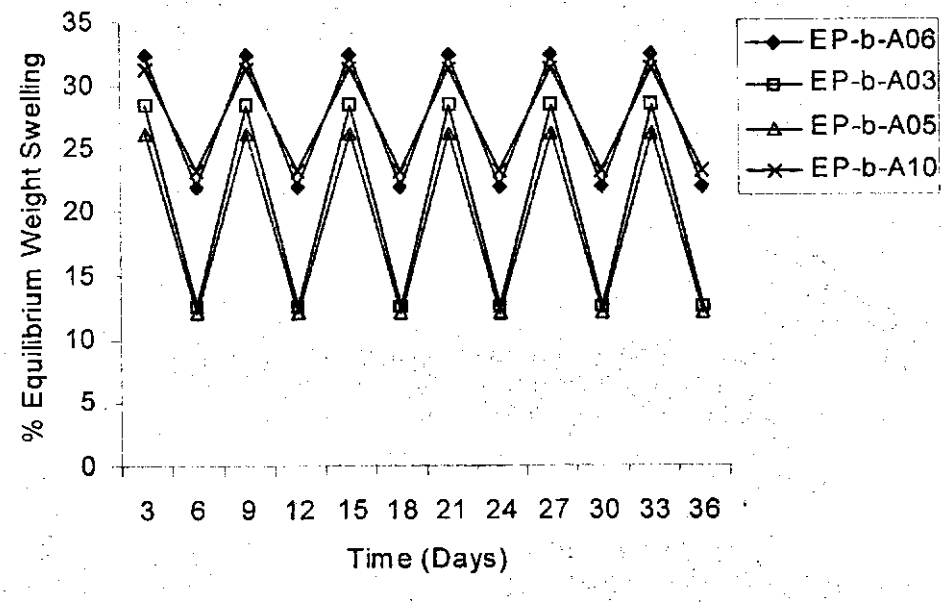


Figure 4 - Oscillatory swelling behavior of epoxy-polyamide/acacia blends polymeric films with pH alternating between 3 and 8. Lower and upper points correspond to pH 8 and pH 3 respectively.

The slight decrease in these values are further observed with a rise in temperature up to 65°C i.e., 6.18, and 5.00 at pH 3 and pH 8 respectively. In this temperature range the expulsion of water from the polymeric film/hydrogel is generally difficult; suggesting that the water remained in the hydrogels was in the form of binding water, referred to as uncontrollable water. However, water adsorbed in the EP-b-A (epoxy-polyamide/acacia) blend polymeric hydrogels is both controllable and uncontrollable water; the controllable water had a characteristic swelling-deswelling ability with the changes in temperature based on the *acacia* content of the systems. From a comparison of Fig 3 (a) & (b) it has been observed that the temperature range where the volume changes are greater (the transition region) is slightly shifted to higher temperatures and is broadened due to more continuous transition as the polymeric gel ionization increases at higher pH.

Buffer type Responsive Characteristics

We also utilized a phosphoric-citric acid buffer with an ionic strength of 0.01 -0.20 M and studied the equilibrium weight swelling behaviour of the previous blends polymeric films over the fixed pH at 3 and 8. The ionic strength was held constant by the addition of sodium chloride. The equilibrium weight swelling characteristics of the blends polymeric films analyzed and compared to the results obtained from the swelling experiments with different buffers for each pH. Table 2 shows the weight swelling ratios of blends polymeric films with 70, 35, 50 and 30 wt. % of Gum *acacia* as a function of pH. The films swelled the most in acidic pH buffer then basic. From a comparison of EWS values especially for EP-b-A (epoxy-polyamide/acacia) blend polymeric film at each pH, it has been observed that, to all ionic strength, phosphate buffer permits greater swelling ratios than citrate buffer and this effect is more pronounced at low ionic strength (0.01 M) and for a completely ionized/ swollen state of systems (pH 3). Thus, at constant ionic strength, phosphate buffer should permit greater swelling than citrate buffer in all cases.

Oscillatory Swelling Behavior

When the completely swollen film is placed in the external solution of pH 8.0, the deswelling process starts with the formation of unchanged and non-ionic shell layer on the surface, and then it gradually moves towards the core region of the film. This dehydrated non-ionic gel layer retards the further release of water as diffusion barrier. This may be the most probable explanation for the slower deswelling process. However, when completely deswollen gel is placed in the acidic medium, a more dehydrated and charge layer is formed on the outermost surface of the gels. The geometrical shapes and forms of the gels were observed to be retained during these cycles. The time domains mentioned in these swelling-deswelling experiments are "significantly controlled by the size and shape of the hydrogels/polymeric films investigated. The smaller the area of the films, the shorter will be the oscillation periods. Therefore, the overall swelling kinetics may be governed by the ion exchange rate.

The oscillatory swelling behaviour of hydrogels/blends polymeric films at 35°C with pH alternating between 3 and 8 was investigated to confirm the reversibility of the swelling process. Figure 4 shows swelling-deswelling behaviour of epoxy-polyamide/acacia blends polymeric films under alternating pH values. The hydrogel was found to undergo a number of swelling-deswelling cycles without undergoing any deformation in its shape. The complete deswelling of the hydrogels were observed to take place in nearly 72 hours, while it required almost 38 hours to swell to the equilibrium in the acidic

solutions of pH 3.0. The difference in swelling and deswelling times can be explained on the basis of the fact that the hydrogels follows different types of mechanisms in the swelling and deswelling process.

CONCLUSION

In conclusion, acacia blends polymeric films swell more in acidic pH solutions than alkaline solutions. The swelling studies show that, pH, temperature, ionic strength and the type of the swelling solution are the basic parameters affecting the equilibrium weight of swelling of epoxy-polyamide/acacia blended hydrogels. Also notable is the fact that addition of only a few percent Gum *acacia* or low polyamide or high epoxy oil content radically changes the swelling behaviour of epoxy-polyamide systems and it become completely a responsive polymer by this modification.

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