"Effect of starch concentration on dielectric properties of Polyvinyl alcohol films"

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I.   INTRODUCTION

Plastic wastes contribute to a significant part of the overall waste volume in municipal landfills and represent a serious environmental concern for the resistance of most synthetic plastics to microbial attack. Plastics represent, however, an integral part of contemporary life and their share in both commodities and high-tech applications is expected to increase in future. Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. Built for long haul, these polymers seem inappropriate for applications in which plastics are used for short time periods and then disposed. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable. In contrast, biodegradable polymers disposed in bioactive environments degrade by the enzymatic action of microorganisms such as bacteria, fungi and algae. Their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. Biodegradable polymers are often derived from plant processing of atmospheric CO_2. Biodegradation converts them to CO_2, CH_4, water, biomass, humic matter and other natural substances. Biodegradable polymers are then naturally recycled by biological process. The world wide consumption of biodegradable polymers has been increasing for last decade, because biodegradable polymers are designed to degrade upon disposal by the action of living organisms. Extraordinary progress has been made in the development of practical processes and products from polymers such as starch, cellulose, gelatin and lactic acid. The need to create alternative biodegradable water soluble polymers for down-the-drain products such as detergents and cosmetics has taken an increasing importance.

To overcome this environment problem, numerous efforts have been made by several research groups in order to produce a noble biopolymer, by blending or filling the natural polymers with other biodegradable synthetic polymers. Starch is often used as a biodegradation additive. The major role of starch has been found to provide higher oxygen permeability as it is consumed by microorganisms [1]. Starch components are more rapidly degrade by microorganism than the synthetic polymers in the blends. Biodegradable materials may be divided into two types, the first type includes starch-filled and second type includes starch-based polymers. The starch content of starch-filled polymers is normally less than 15% by weight. In traditional plastics, particularly in poliolefins such as starch/ high density polyethylene, starch is used as natural filler. These films biodeteriorate on exposure of microbial environments [2-4]. Starch based polymers contain relatively higher percentage of starch (more than 40% by weight), mixed with synthetic polymers. It makes them attractive for biodegradability and several blends have been prepared and tested for packaging applications. The range of mechanical properties of these polymers falls short of the required properties, but improvements have been made by blending, co-polymerization, grafting and cross-linking [2-5].

Although most of the synthetic polymers cannot be recycled, environmental pollution caused by them is becoming more and more serious. To overcome this problem, numerous efforts have been made to develop environment friendly biodegradable polymers in recent years [6,7]. Recently many efforts have also made to blend natural polymers, like starch, cellulose, gelatin with synthetic polymer like PVA, which is recognized as a biodegradable polymer and its biodegradation in various microbial environment have been reported [8,9]. PVA is a non-toxic, water-soluble synthetic polymer, which has been employed in biomaterial technology for the pharmaceutical and biomedical areas due to its excellent film-forming, emulsifying and adhesion properties [10]. The PVA is obtained by hydrolysis of poly (vinylacetate), then different types of PVA can be produced depending on the degree of hydrolysis involved. The degree of hydrolysis of PVA can affect the physical properties of this polymer and its films [10].

Tudorachi *et al.* [11] have studied the mechanical properties, thermal behaviour and biodegradation of some polymeric materials based on PVA and starch, in the presence of urea and glycerin. Jayasekara *et al.* [12] have prepared several blend of PVA, starch and glycerol. They studied surface modification of solution cast starch PVA blended films.

The chemical structure (responsible for functional group-stability, reactivity, hydrophilicity and swelling behaviour) is the most important factor affecting the biodegradability of polymeric materials. Other important

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factors are inter alia, physical and physico-mechanical properties, e.g. molecular weight, porosity, elasticity and morphology (crystalline, amorphous) [13,14].

However, more data on the physical properties of films based on blends of PVA and starch, produced by casting, are necessary. Thus the objective of this study was the development of biodegradable films based on blends of starch and PVA, with no plasticizer and the characterization of their dielectric studies on behalves of the parameters like dielectric permittivity, dielectric loss, ac conductivity, relaxation time, loss tangent, extinction coefficient and refractive index. The dielectric properties of PVA are considered to be a good tool for studying the polarization as well as molecular relaxation mechanisms dealing with the dynamics of mobile groups. Hence it is very important to examine the dielectric properties of PVA as a result of the variation of its molecular motion, which is affected directly by starch concentrations.

II.   EXPERIMENTAL

The films of virgin PVA and its composites with different additives selected for the study, were prepared in the laboratory by weight percentage method using solution cast technique [15-19]. PVA films doped with different mass fractions of the dopant (wt%) were prepared by using the relation

$$M(wt\%) = \frac{m_d}{m_p + m_d} \times 100$$

where m_d and m_p are the weight of dopant and polymer, respectively. Initially PVA was dissolved in deionized water then the required amounts of additives were added into the solution for the preparation of films of varying weight percentages. It is usually important in dissolving polymers to have the materials as finely divided as possible and to have each particle thoroughly wetted by the solvent. Agitation of some kind is important, since the solvent penetration is very slow for high molecular weight polymers and a viscous coating is usually formed over each particle, which retards further solvent diffusion into the polymer. The solution was stirred by a magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution. The well dispersed and homogenously mixed solution was poured into a flat-bottomed cleaned petri-dish. The petri-dish containing solution was floated over a pool of mercury to ensure the uniformity in the thickness as shown in Figure 1.

Figure 1:-Schematic figure of the petri dish
floating on a mercury tray

The solution was then placed in a dust-free chamber and allowed to evaporate slowly over a period of 4-5 days at room temperature. The film so obtained was peeled off. The average thickness of the prepared films was found of the order between 100-110 μm. Micrometer (Mitutoyo, Japan, M120-25) with a least count of 1 μm was used in order to measure the thickness of the films. The films cut into pieces of suitable size for the measurement of their various properties.

Sample preparation

Polymeric films of virgin PVA and doped PVA with biopolymers were prepared using solution cast method as described earlier.The starch was taken in percentage weights viz. 4%, 6%, 8% and 10%, in order to prepare the PVA films filled with starch. The average thickness of all the prepared films was of the order of 100 μm.

Dielectric measurements

All the prepared polymeric films of virgin PVA and filled PVA with starch or gelatin, were subjected to measure their dielectric parameters at microwave frequency in X-band, using the technique developed by Dube and Natarajan [20].

III.   Results And Discussion
Dielectric relaxation studies of pure PVA and doped PVA with starch composite films
In Table 1, dielectric permittivity (ϵ') , dielectric loss (ϵ''), ac conductivity (σ'), relaxation time (τ), loss tangent (tanδ), extinction coefficient (k) and refractive index (n) evaluated for pure PVA and its composite with starch at 9.03 GHz frequency and at room temperature (35^0C) for the film of varying concentrations, are listed.

Table 1:- Dielectric parameters, dielectric permittivity (ϵ'), dielectric loss (ϵ''), ac conductivity (σ'), relaxation time (τ), loss tangent (tanδ), extinction coefficient (n) and refractive index (n), carried out for PVA and PVA/starch composite films at 9.03 GHz frequency and at room temperature (35^0C)

Sample	Dielectric constant ϵ'	Dielectric loss ϵ''	ac conductivity σ' (Sm^{-1})	Relaxation time τ (10^{-12})Sec.	Loss tangent tanδ	Extinction coefficient k	Refractive index n
Pure PVA	3.07	0.72	0.36	4.1	0.23	0.11	1.76
PVA+4%Starch	3.20	1.06	0.53	5.8	0.33	0.16	1.81
PVA+6%Starch	3.21	1.34	0.67	7.4	0.42	0.20	1.83
PVA+8%Starch	3.23	1.53	0.77	8.3	0.48	0.22	1.85
PVA+10%Starch	3.26	1.66	0.83	9.0	0.51	0.24	1.86

Dielectric permittivity (ϵ') for pure PVA and its composites with starch was obtained in the range 3.07-3.26 and dielectric loss (ϵ'') was obtained in the range 0.72-1.66 for the film having thickness of the order of 100 μm. The SEM analysis investigated by Azahari *et al.* [21] on PVA and starch composite films reveal that as the starch content increased, the starch phase changed from the dispersed phase, which indicates that amorphous starch is partially miscible with PVA. In general, in the case of heterogeneous mixture the behaviour of dielectric properties is governed by Maxwell-Wagner-Siller model [22]. As per this model it is predicted that the value of dielectric constant increases with the increase in concentration as well as conductivity of the inclusion. As PVA and starch make heterogeneous mixture [21], the results of the present study show an increasing trend in the dielectric parameters accordingly.
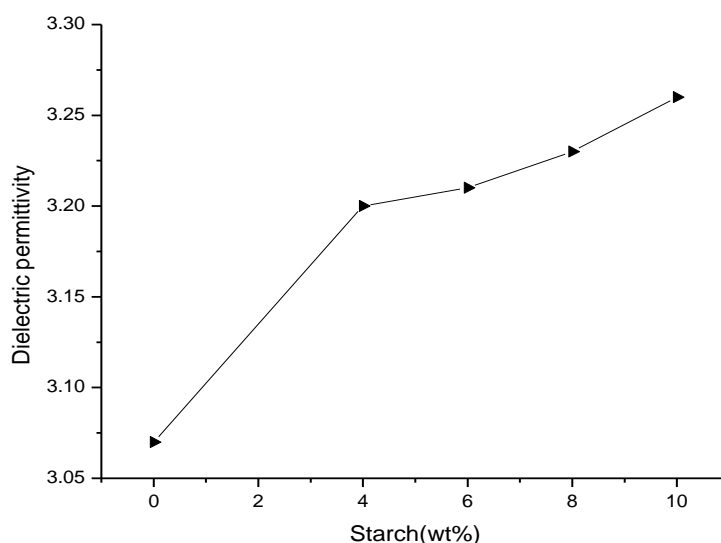

Figure 2:- Variation of dielectric permittivity (ϵ')with doping percentage of Starch in PVA

Table 1 and Figure 2 depict the variation of dielectric permittivity (ϵ') for all types of prepared composite films at constant temperature (35^0C). Omed *et al.* [23], evaluated dielectric constant of PVA at lower frequency range (10 KHz-1MHz) and at different temperature. At 30^0C temperature and 10 KHz frequency, ϵ'

for pure PVA is quite higher and showed decreasing slightly upto 1 MHz frequency. The value of ϵ' remains around 5.0 for the entire frequency range at 30^0C temperature. As we have been used microwave frequency (9.03 GHz), the ϵ' obtained for pure PVA is 3.07, which is according to the decreasing trend of the value of ϵ', with increase in frequency. The variation in the dielectric parameters with frequencies can be explained in terms of the relaxation time (τ); at low frequencies, the electric dipole have sufficient time to align with the field before the field changes its direction, consequently the dielectric constant is high. At intermediate frequencies the dipoles move but have not completed their movement before the field changes direction and they must realign with changed field, at very high frequencies (like our case), the ϵ' decreases due to the shorter time available for the dipole to align. The relaxation time (τ) evaluated and it was found of the order of pico second and in the range 4.1-9.0 for pure PVA and its composites with starch (Fig. 3), were in accordance with the above theory. Our dielectric parameters for pure PVA followed by Raja *et al.* [24].
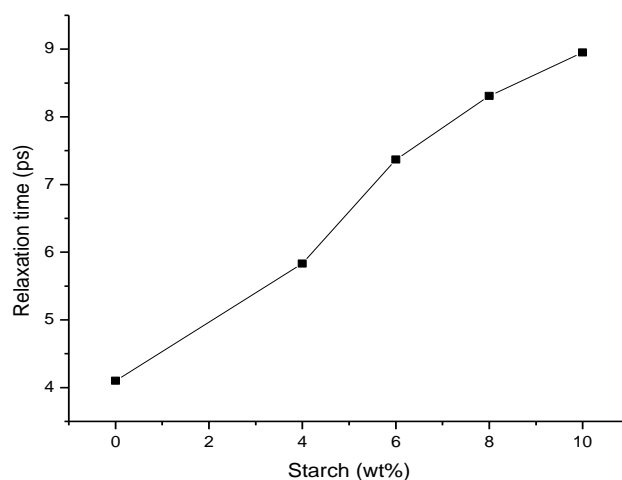

Figure 3:- Variation of relaxation time (τ)with doping percentage of Starchin PVA

The dielectric loss (ϵ'') obtained for PVA is 0.72 and for its starch composite films it varies from 1.06-1.66 (Fig. 4). The higher value of ϵ'' for the higher concentration of dopant can be understood in terms of ac conductivity (σ'), which is associated with ϵ''.
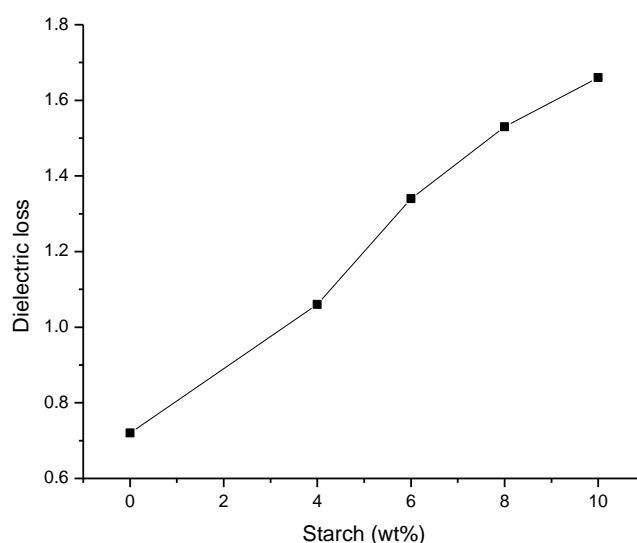

Figure 4:- Variation of dielectric loss (ϵ'') with doping percentage of Starchin PVA

The ac conductivity (σ') obtained for neat PVA to be 0.36 Sm^{-1} and for its starch composite films, σ' varies from 0.53-0.83 Sm^{-1} (Fig. 5). PVA exhibits flexible polar side groups with polar bond, as the bond rotating having intense dielectric α- transition [25]. Thus there is a change in the chemical composition of the

polymer repeated unit due to the formation of hydrogen bonds with hydroxyl groups in the polarization process, which in turns makes the polymer chain flexible and enhances the electric conductivity and hence dielectric losses accordingly.
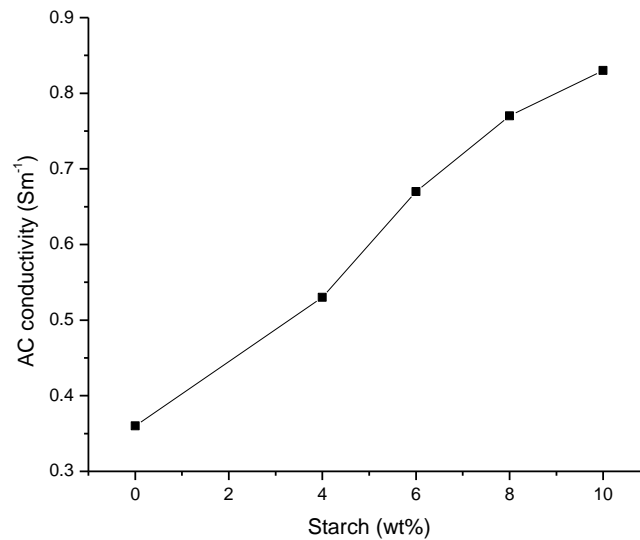

Figure 5:- Variation of ac conductivity (σ')with doping percentage of Starchin PVA

Loss tangent ($\tan\delta$) for pure PVA and PVA/ Starch composite films has been obtained in the range 0.23-0.51. The variations in the value of loss tangent ($\tan\delta$) with varying doping concentration are shown in Figure 6. The origin of microwave dielectric loss in polymer are attributed to dipole absorption dispersion in both crystalline and amorphous polymers, dipolar losses due to impurities and photon-phonon absorption spectra corresponding to the density of states in amorphous regions of polymer [26].
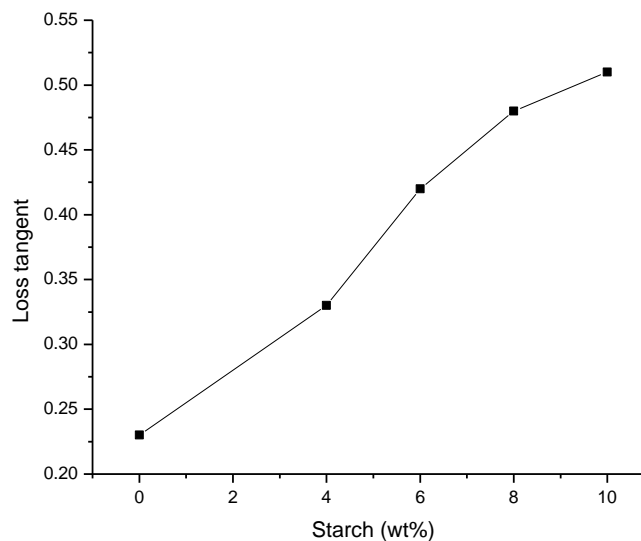

Figure 6:- Variation of loss tangent ($\tan\delta$)with doping percentage of Starchin PVA

The optical constants viz., extinction coefficient (k) and refractive index (n) have been obtained. For pure PVA, k comes out to be 0.11 and for its composite films with starch, k varies in the range 0.16-0.24. The values of n are found to be lie in the range 1.76-1.86 for PVA and PVA/ starch composite films. The variation of k and n with different starch concentration in PVA are shown in Figure 7 and 8 respectively. The significance of k is given by the fact that after the wave has travelled over a distance equal to the wavelength of wave in the dielectric material, its amplitude decays by a factor$e^{-2\pi k}$.
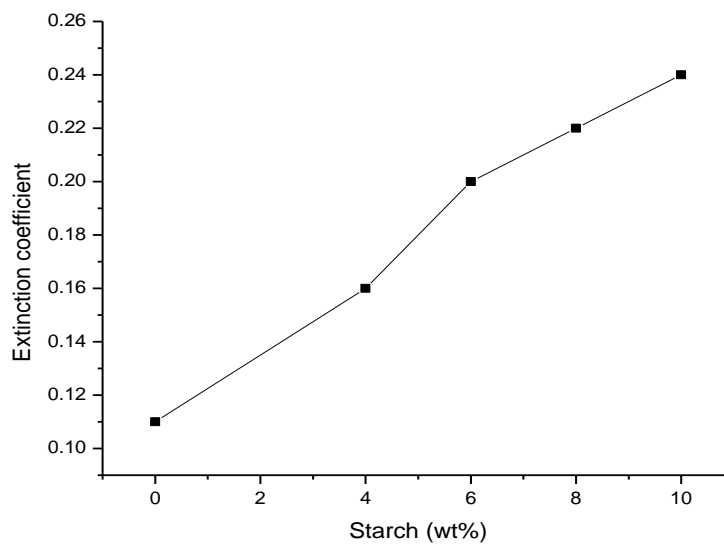
Figure 7:- Variation of extinction coefficient (k) with doping percentage of Starchin PVA
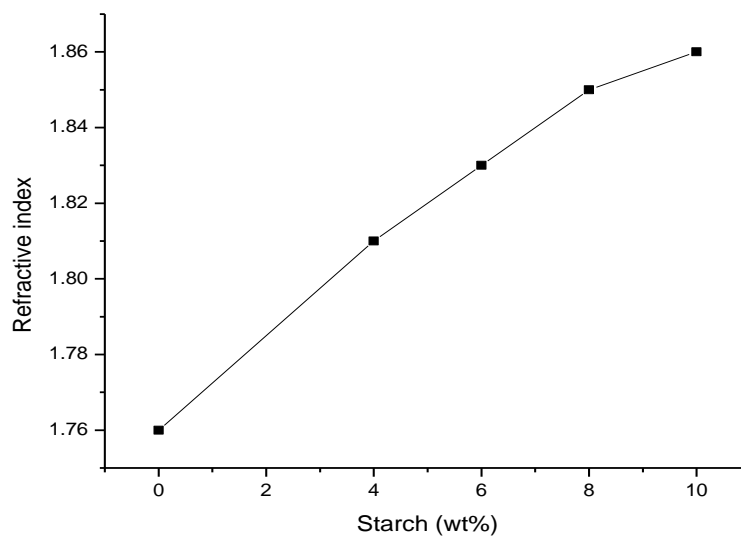

Figure 8:- Variation of refractive index (n) with doping percentage of Starchin PVA

As PVA and starch composite has been established as completely biodegradable materials and are widely used in pharmaceuticals microbial and food industries. The dielectric parameters listed in Table 1, which enhance with the addition of starch into PVA matrix. Hence their application in electrical appliances may be useful in order to reduce environmental pollution, as compared to other synthetic non-biodegradable polymers.

IV.   Conclusion

• The dielectric parameters carried outat microwave frequency (9.03 GHz) and at room temperature for pure PVA and PVA-starch composite films, have been found to show incremental values. The ϵ' varies from 3.07-3.26 and ϵ'' from 0.72-1.66, as starch content increases into PVA matrix. The loss tangent is found to vary from 0.23-0.51, thus having good microwave lossy behavior.

• The present study of PVA host and its starch composite films reveal that PVA can be effectively combine with starch to enhance its dielectric parameters such as ac conductivity, relaxation time, extinction coefficient and refractive index obtained for the samples under investigation, and alter their conduction behaviour.

• Blending starch with PVA to produce biodegradable composite materials with adequate dielectric properties could be a practical way to reduce environmental pollution.

- Being an electrodeless technique, measurements at microwave frequencies are free from electrode polarization and associated problems and thus yield real material parameters.

References

[1]. M Rutkowska, A Heimowska, K Krasowska and H Janik, *Polish J. of Environ. Studies*, 11(2002) 267.
[2]. R Jayasekara, I Harding, I Bowater and G Lonergan, *J. Polymer Environ.*, 13(2005) 231.
[3]. A C Albertsson, *Eur. Polymer J.*, 16(1980) 623.
[4]. R Chandra and R Rustgi, *Polymer Degrad. Stabil.*, 56(1997) 185.
[5]. C Huang, A S Shetty and M S Waug, *Polymer Technol.*, 10(1990) 23.
[6]. I S Arvanitoyannis, *J. Macromol. Sci. Rev. Chem. Phys.*, 39(1999) 205.
[7]. G J Dong, *Int.Biodeter. Biodegr.*, 52(2003) 69.
[8]. B L Lopez, A I Mejia and L Sierrs, *Polym. Eng. Sci.*, 39(1999) 1346.
[9]. A Corti, R Solaro and E Chiellini, *Polym. Degrad. Stabil.*, 75(2002) 447.
[10]. C A Finch, *Polymers*, 5(1983) 81.
[11]. N Tudorachi, C N Cascaval, M Rusu and M Pruteanu, *Polymer Testing*, 19(2000) 785.
[12]. R Jayasekara, I Harding, I Bowater, G B Y Christie and G T Lonergan, *Polymer Testing*, 23(2004) 17.
[13]. M Acemoglu, *Int. J. Pharm.*, 277(2004) 133.
[14]. J M Anderson and M S Shive, *Adv. Drug Deliv. Rev.*, 28(1999) 5.
[15]. A Rawat, H K Mahavar, S Chauhan, A Tanwar and P J Singh, *Indian J. Pure & Appl. Phys.*, 50(2012) 100.
[16]. A Tanwar, K K Gupta, P J Singh and Y K Vijay, *Bull. Mater. Sci.*, 29(2006) 181.
[17]. A Tanwar, K K Gupta, P J Singh and Y K Vijay, *Bull. Mater. Sci.*, 29(2006) 397.
[18]. S D Yoon, S H Chough and H R Park, *J. Appl. Polym. Sci.*, 100(2006) 2554.
[19]. S Agrawal, S Srivastava, S Kumar, S S Sharma, B Tripathi, M Singh and Y K Vijay, *Bull. Mater. Sci.*, 32(2009) 569.
[20]. D C Dube and R Natarajan, *J. Appl. Phys.*, 44(1973) 4927.
[21]. N A Azahari, N Othman and H Ismail, *Journal of Physical Science*, 22(2011) 15.
[22]. P Hedying, *Dielectric Spectroscopy of Polymers* (Bristol: Helger) (1977) p 28.
[23]. G A Omed, K A Bakhtyar and O S Alan, *International Journal of Science and Advanced Technology*, 2(2012) 65.
[24]. V Raja, A K Sharma and V V R N Rao, *Materials Letters*, 58(2004) 3242.
[25]. K P Singh and P N Gupta, *European Polymer Journal*, 34(1998) 1023.
[26]. A Eftekhari, A K St. Clair, D M Stoakley, S Kuppa and J J Singh, *J. Polym. Mater. Sci. Eng.*, 66(1992) 279.