

Reaction and functionality of sulfuric and chromic acids over low density polyethylene for medical textiles: A comparative study

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Abstract - Low density polyethylene (LDPE) swollen in mixture of polar and non-polar solvents was subjected to sulfuric and chromic acids to promote durable hydrophilic and electrical properties. ATR-Fourier transforms infrared spectroscopy and elemental analysis of the treated LDPE depicts the reaction mechanism of both the acids over low density polyethylene in swollen condition. Both sulfuric and chromic acids promote in-depth modification of LDPE resulting in enhanced hydrophilicity and lower electrical resistivity of the polymer. FTIR spectra indicate formation of double bonds, sulfonic and carbonyl moieties. Contact angle goniometry indicates a 30° decrease in contact angle and Photo Luminescence Spectroscopy computes band gap decrease to 2.8eV. Comparative results suggest chromic acid as more influential functionalization agent for low density polyethylene at lower concentrations.

Index Terms - Low density polyethylene, mineral acids, reaction mechanism, hydrophilicity, band gap.

1 INTRODUCTION

Surface treatment employing chemicals and radiations sources are normal industrial practices to improve hydrophilicity, adhesion, biocompatibility and biodegradability of polyethylene films. These properties are desirable for better printing of polymer films and many specialized products ranging from electrochemical to medical industries [1],[2],[3],[4],[5],[6]. Surface modification introduces functional groups moieties and changes in surface morphology. One of the main techniques used for surface modification of polymer films is wet chemical treatment which employs mainly oxidizing agents under different reaction conditions [7],[8],[9]. Generally polyolefins are used in the packaging industry and most of the research reported, concerns surface treatment of films [10]. However, not much work has been carried out on the bulk treatment of polyethylene for applications in other forms such as fibers, yarns and sheets. LDPE is the highest produced commodity polymer offering higher reactivity, comparatively lower electrical resistivity than its other polyolefin counterparts. With low cost and ability to form various shapes, it is a good candidate for medical textile material applications. In a previous study, we have customized a liquid phase functionalization process for in-depth modification of LDPE using mineral acids under action of solvents [11]. This study compares the

impairing agents and also explores the interaction of sulfuric and chromic acid with polyolefins. Introducing functional groups via oxidation using chromic acid was first done by Rasmussen at 25°C and 75°C producing 60% carboxylic and 40% aldehyde and ketone functional groups at surface of LDPE film [12]. Idage and Ihata used fuming sulfuric acid as functionalizing agent over LDPE film producing sulfonic acid groups with polyene linkages for improved hydrophilicity [13],[14]. Fonseca et al. demonstrated that sulfuric acid action over polyethylene reduces its electrical resistivity [15]. Characterizing the effect of annealing and rate of reaction on polyolefin film, Bergbreiter and Tada applied fuming and concentrated sulfuric acid in order to functionalize the polymer [16],[17]. Fischer compared the results of LDPE sulfonation using fuming sulfuric acid after 5 and 80 minutes and concluded that after 5 minutes surface sulfonation is nearly complete and during extended reaction time sulfonation in the bulk polymer is initiated [18]. According to both Kaneko and Gordon, sulfonation reaction proceeds with the abstraction of hydrogen atom of the C-H group from the main chain C-C backbone or from the methyl group -CH₃ and it is replaced by the sulfoxide group, which is subsequently hydrogenated to form a sulfonic group on carbon atom. Finally desulfonation occurs due to abstraction of hydride ion forming double bonds in the polyethylene chain. In the case of fuming sulfuric acid after the abstraction reaction, these double bonds react with SO₃, resulting in the production of alkene sulfonic acids and sultones [19],[20],[21]. As far as chromic acid in addition to sulfonation reaction is concerned, the dichromate ion undergoes a reaction with polyethylene forming chromium ester intermediate, which is hydrolyzed to alcohol. Subsequently in acidic solution primary alcohols oxidizes to carbonyl functional groups [22],[23]. Considering inherent properties of LDPE, bulk sulfonation was carried

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performance of sulfuric and chromic acids as functionality

out using swelling technique to improve its dye receptivity, hydrophilicity and electret properties for its intended application in medical textiles [11]. As anticipated, sulfonation reaction remained electrophilic in nature [19],[20],[21]. Proposed reaction mechanisms of sulfuric and chromic acids with LDPE for liquid phase process are based on the available literature, infrared spectroscopy and elemental analysis. Contact angle goniometry determines hydrophilic properties with respect to the acid concentration. As photo emission spectroscopy indicates a marked decrease in band gap energy level, electron transport appears to be facilitated through conjugated double bonds produced after acid treatment of low density polyethylene.

2 EXPERIMENTAL

In this section, we illustrate the LDPE functionalization procedures, instruments and techniques used for the determination of chemical and functional properties of the sulfuric and chromic acid treated LDPE.

2.1 Materials and Procedure

LDPE pellets (Petlin Malaysia Sdn Bdh) were used for functionalization. Analytical grade sulfuric acid (96%) and potassium dichromate (Fischer Scientific Malaysia) were used to make 2.5, 5, 10 and 15 M sulfuric acid and chromic acid solutions with deionized water.

2.2 Sample Preparation

The treated polyethylene samples were designated as SAE 2.5M, SAE 5.0M, SAE 10.0M, SAE 15.0M and as CAE 2.5M, CAE 5.0M, CAE 10.0M, CAE 15.0M. SAE and CAE stands for sulfuric acid chromic acid treated entities and numeric value illustrates the molarity of acid used over the low density polyethylene.

2.3 Elemental Analysis

Simultaneous determination of carbon, hydrogen, sulfur and oxygen content was carried out using Vario MACRO Cube elemental analyzer.

2.4 Fourier Transform Infra-Red Spectroscopy

Attenuated total reflectance (ATR) Fourier Transform Infra-Red spectroscopy was done using Perkin Elmer Spectrum 100 apparatus.

2.5 Contact Angle

Treated polyethylene samples were heated in order to make films and contact angles for double distilled water droplets

were taken at least on eight different spots. Angles were measured at 25°C using a goniometer 14° horizontal beam comparator from KRÜSS, GmbH, Germany.

2.6 Photo Luminescence Spectroscopy

Electron band gap values were determined at room temperature of 25°C for the treated samples using LP920 photo luminescence spectrometer from Edinburgh Instruments.

3 RESULTS AND DISCUSSIONS

3.1 Elemental Analysis

Analysis of carbon, nitrogen, hydrogen, oxygen and sulfur of treated LDPE in powder form was performed using the elemental analyzer. The relative change in the elemental percentages given in Table 1 shows the effect of increasing concentration of sulfuric and chromic acids on LDPE. The elemental data shows that carbon content, which is about 85% in pure LDPE, decreased to 73 and 63% level for sulfuric and chromic acid treated LDPE, respectively. Similarly, respective oxygen percentages rose to 11% and 20% from a negligible amount indicating a sharp decrease in carbon to oxygen ratios. This increase of number of oxygen per carbon atom indicates oxidation resulting in the formation of carbonyl functional groups. Similar rise in sulfur percentage also indicate formation of sulfonic functional groups. Elemental ratios for LDPE illustrated in Table 2 indicate the relative decrease in carbon to hydrogen ratio and this gives a good indication of double bond formation on the polymer main chain with proportional increase in acid concentration. The presence of 0.16 and 0.34 oxygen atoms per carbon atom in the treated LDPE indicate the extent of oxidation in the polymer treated with sulfuric acid and chromic acid. These results also support the increase in the density of LDPE observed for the respective functionalized polymers.

TABLE 1: Elemental percentage of sulfuric and chromic acid treated LDPE.

Sample Name	C (%)	H (%)	S (%)	O (%)
LDPE	85.60	14.30	0.01	0.01
SAE 2.5	84.06	14.24	0.23	1.45
CAE 2.5	77.82	13.75	0.82	7.60
SAE 5.0	75.11	13.51	0.36	10.90
CAE 5.0	72.63	13.25	1.51	12.56
SAE 10.0	73.82	13.71	0.72	11.05
CAE 10.0	65.47	12.50	2.72	19.32
SAE 15.0	73.28	13.37	1.35	11.98
CAE 15.0	63.65	13.02	1.45	20.57

TABLE 2: Elemental ratios of sulfuric and chromic acids treated LDPE.

Sample Name	S/C	O/C	C/H
SAE 2.5	0.0028	0.0172	5.9036

CAE 2.5	0.0106	0.0977	5.6613
SAE 5.0	0.0048	0.1465	5.5616
CAE 5.0	0.0208	0.1729	5.4657
SAE 10.0	0.0098	0.1588	5.4809
CAE 10.0	0.0415	0.291	5.151
SAE 15.0	0.0184	0.1635	5.3843
CAE 15.0	0.0227	0.3431	4.888

3.2 Fourier Transform Infra-Red spectroscopy

Infrared spectroscopic changes were used to identify sulfonation and carbonyl functional groups formation. Important functional groups which arise due to the action of sulfuric and chromic acid in polyolefin include the following: Transmittance bands between 840 and 1250 cm^{-1} are ascribed to sulfonic groups. Other bands in the region of 1500 to 1800 cm^{-1} are assigned to olefinic double bonds and carbonyl groups i.e. ketones, aldehydes and carboxylic acids. Dual peaks in the region 2800-2950 cm^{-1} corresponds to alkene C-H stretch. Lastly the broad band occupying 3100-3600 cm^{-1} is referred to the presence of hydroxyl group [24]. Tables 3 and 4 illustrate important functional groups, their vibration type and range and percentage increase in transmittance intensity due to increase of acid concentration over LDPE.

Table 3: Percentage Intensity increase of LDPE treated with sulfuric acid.

Functional groups and Wavelength	S=O 1030~ 1050	C=C 1630~ 1690	C-H 2800~ 2950	OH 3100~ 3600
SAE 2.5M	5.88	4.85	13.72	6.86
SAE 5.0M	7.84	9.80	14.71	21.57
SAE 10.0M	4.90	10.78	15.69	22.55
SAE 15.0M	9.80	6.86	14.80	16.67

Table 4: Percentage Intensity increase of LDPE treated with chromic acid.

Functional groups and Wavelength	S=O 1030~ 1050	C=C 1630~ 1690	C=O 1680	OH 3100~ 3600
CAE 2.5M	6.86	4.90	3.92	9.80
CAE 5.0M	7.85	5.88	4.90	10.7
CAE 10.0M	11.8	7.84	6.86	15.7
CAE 15.0M	4.90	5.88	N/A	13.7

3.3 Chemical reaction of sulfuric acid with LDPE

Gordon and Main supports the formation of double bonds, with evolution of sulphur dioxide and carbon dioxide [20],[21]. Kaneko et al suggest that the SO^3 present in oleum reacts with the double bonds resulting in production of sultones, sulfonic acid and other sulphate groups [19]. Mechanism of the reaction between LDPE and diluted sulfuric acid is illustrated in Figure 1. The proposed scheme

is based on the results obtained from the FTIR and elemental analysis of the treated samples. The reaction scheme shows that $\text{SO}_2\text{-OH}$ becomes part of the side chain of polyethylene after electrophilic substitution to a carbon atom.

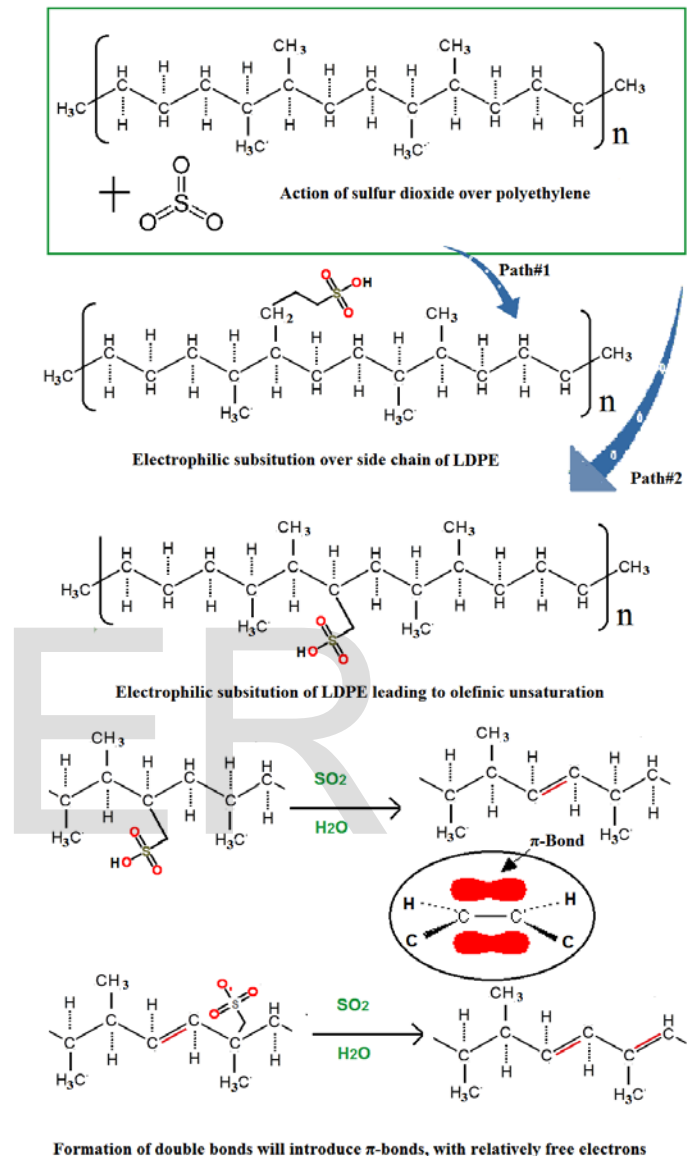


FIGURE 1: Proposed reaction mechanism of sulfuric acid with LDPE in gel form.

The second possible step is attachment of $\text{SO}_2\text{-OH}$ to the main chain of polyethylene after electrophilic substitution to a carbon atom thus becoming part of the main chain. An extension of the second step is that the main chain sulfurous acid attacks the neighboring hydrogen, abstracting a hydride ion and thus resulting in the formation of carbon to carbon double bond. These sulfonation and de-sulfonation reactions are enhanced with time and also when the temperature is increased.

3.4 Chemical reaction of chromic acid with LDPE

It is known that chromic acid, in addition to the sulfonation reaction, adds carbonyl functional groups to LDPE by replacing hydrogen from the polymer main chain. The proposed reaction mechanism between LDPE and chromic acid is illustrated in Figure 2. It is desirable that the solvents should not react with the acids. In the earlier case, as discussed, there was no reaction between cyclohexane and sulfuric acid or between ethanol and sulfuric acid. However, when chromic acid was used it was observed that ethanol reacted with sulfuric acid and potassium dichromate, resulting in the formation of potassium sulfate, dichromic acid and aldehyde ethanal intermediates. At this stage the color of chromic acid changed from orange to green. We postulate that aldehyde ethanal is saturated to form a primary alcohol and the resulting dichromic acid disassociates into chromic acid and water. The main reaction commences with the action of chromic acid with polyethylene forming chromium ester intermediates. These intermediates are finally hydrolyzed to hydroxyl functional moieties. In all the resulting hydroxyl functional groups are converted into carbonyls such as aldehydes, ketones and carboxylic acid.

3.5 Contact Angle

Surface of the functionalized LDPE establishes better hydrogen bonding with water droplet, consequently spreading it over polymer surface and lowering contact angle of polymer [25],[26]. The hydrophilic behavior of the functionalized LDPE was measured by grinding and hot pressing at a temperature of 130°C for five minutes to produce 2mm thick films for contact angle analysis. Table 5 compares the contact angle values of sulfuric and chromic acid treated low density polyethylene with virgin LDPE. Best wetting performance obtained was 64° and 62° at 15.0M concentrations for sulfuric and chromic acid treated LDPE. Integration of functional group moieties into LDPE is indicated by a substantial decrease in the contact angle from initial value of 99° for the untreated LDPE. Overall results indicate similar trend for the LDPE samples treated with both acids. Almost linear decrease in the contact angle values was observed as the concentrations of the acids were increased thus demonstrating that the desired level of hydrophilicity can be imparted to LDPE by controlling the acid concentration in the liquid phase.

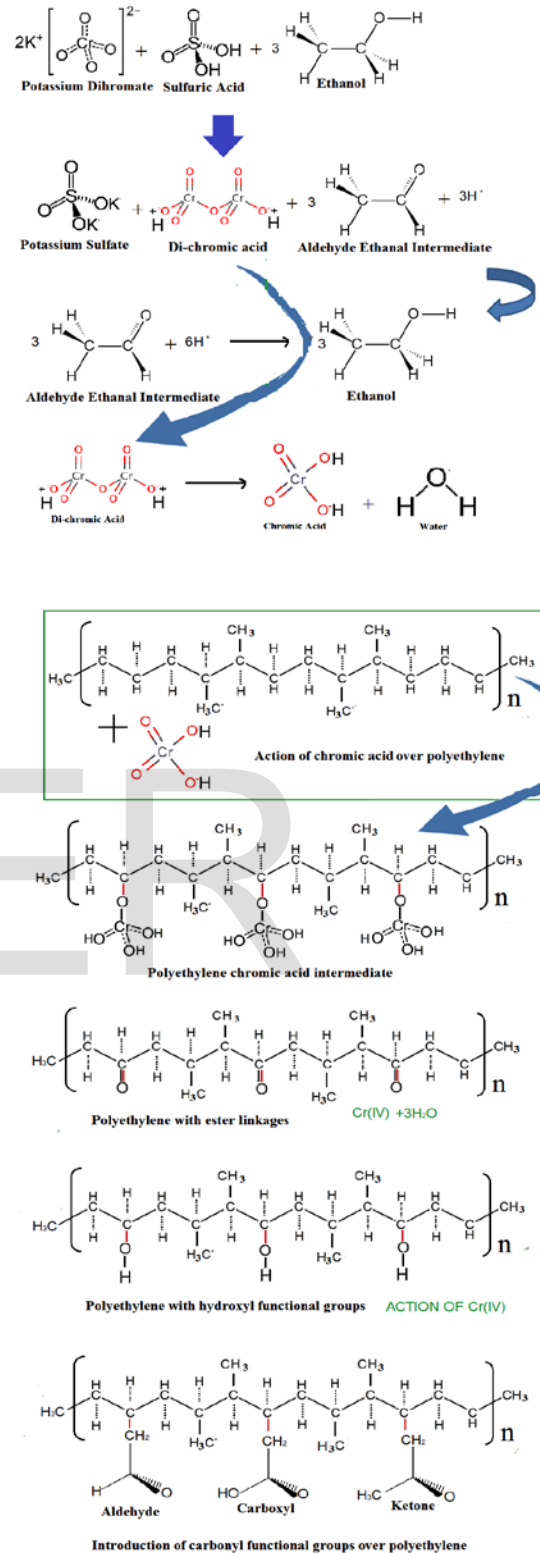


FIGURE 2: Proposed reaction mechanism of chromic acid
 Table 5: Contact angle for sulfuric and chromic acids treated LDPE.

Sample name	Contact angle °θ	Sample name	Contact angle °θ
LDPE	99.0		
SAE2.5M	80.1	CAE2.5M	77.3
SAE5.0M	71.2	CAE5.0M	75.9
SAE10.0M	70.9	CAE10.0M	71.4
SAE15.0M	64.7	CAE15.0M	62.6

3.6 Photo Luminescence Spectroscopy

Photo-emission spectra were obtained for both sulfuric and chromic acids treated LDPE in ultra violet region under vacuum. There is low mobility of carriers in the pristine polyethylene, with reported values of photoconduction ranging from 7 to 14eV with average value of 8.5eV [27],[28]. As illustrated in Figure 3 the acid treated LDPE exhibited a considerable reduction in the band gap value as the concentration of the acid treatment was increased.

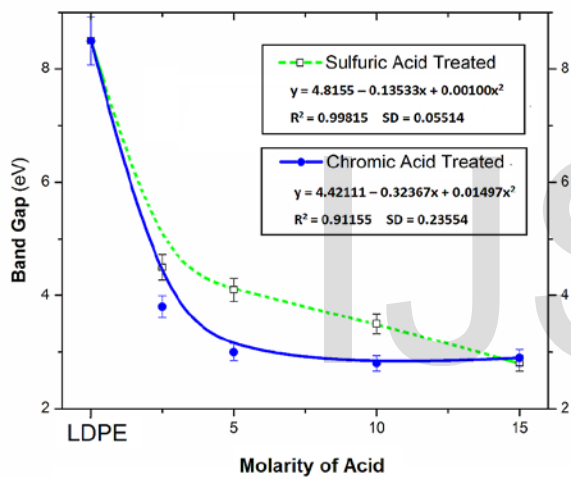


FIGURE 3: Band gap values for treated LDPE with sulfuric and chromic acids respectively.

The photo currents are mainly generated due to the rapid motion of carriers through polyethylene chain due to the formation of double bonds within LDPE structure. The lowest electron band gap value of 2.8eV±0.2eV was obtained for the 15M sulfuric acid treated LDPE sample. However, similar results were obtained for chromic acid treatment where band gap decreased to 2.8eV only at 10.0M treated LDPE sample. Electron transport appears to be facilitated through conjugated double bonds produced after acid treatment of low density polyethylene.

4 CONCLUSIONS

A comparative study of varying concentrations of sulfuric

and chromic acids on low density polyethylene in bulk sulfonation was carried out. ATR-Fourier transforms infrared spectroscopy, and elemental analyses of the treated LDPE samples show that chromic acid treatment is more effective than sulfuric acid treatment for functionalization of the polymer at lower acid concentrations. Marked decrease in contact angle and band gap energy values point toward hydrophilic and conducting nature of the modified LDPE. Since, functionalization of LDPE in the bulk leads to enhanced hydrophilicity and superior electrical properties. It can be concluded that both sulfuric and chromic acids improves formation of double bonds and accumulation of carbonyl and sulfonic groups in treated LDPE for considerable applications in medical textiles.

REFERENCES

- [1] S. Vasconcellos, J. A. P. Olivera, R. Neto, Euro Poly J., 1997, 33, 1731-1734.
- [2] P. Blais, D.J. Carlsson, G. W. Csullog, D. M.Wiles, J. of Colloid Interface Sci, 1974, 47, 636-649.
- [3] R.B. Cheikh, P.A. Askeland, R.L. Schalek, L.T.Drzal, J. Adhes Sci Technol, 2002,16, 1651.
- [4] S. Banisadr, H. Asempour, Iran. J of Polym Sci. 2012, 21: 463-471.
- [5] E.V. Kuvelidna, T.G. Shikova, S.A. Smimov, V.V. Rybkin, High Energy Chem., 2007, 41: 284-287.
- [6] P.K. Roy, P. Surekha, C. Rajagopal, J. of Appl. Polym. Sci., 2011, 122, 2765-2773.
- [7] S. Bentjen, D. Nelson, B. Tarasevich, J. Appl. Polym. Sci., 1992, 44, 965-980.
- [8] E. Kontou, M. Niaounakis, Polym., 2006, 47, 1267-1280.
- [9] A.A. Basfar, K. M. Idriss Ali, Polym. Degr. and Stab. 2006, 91, 437-443.
- [10] V. Cornelia, P. Mihaela, Practical Guide to Polyethylene, 2005, Rapra Tech.
- [11] M.R. Kazimi, T. Shah, S. S. Jamari, I. Ahmed, C. K. Mohammad Faizal, Poly. Engg and Sci., 2014, 54, 2522-2530.
- [12] J. R. Rasmussen, E. R. Stedronsky, G. W. Whitesides, J. of Am Chem. Soc, 1977, 99, 4737-4745.
- [13] S. B. Idage, S. Badrinarayanan, S. P. Vernekar, S. Sivaram, Langmuir, 1996, 12, 1018-1022.
- [14] J.Ihata, J Polym Sci, Part A: Polym Chem, 1988,26, 167-176.
- [15] Fonseca, J. M. Perena, J. G Fatou, Bello, J. of Mat Sci. 1985, 20, 3283-3288.
- [16] Bergbreiter, K. Kabza, J. Am. Chem. Soc. 1991,113, 1447-1448.
- [17] H. Tada, S.Ito, Langmuir, 1997, 13, 3982.
- [18] Fischer, H. Eysel, J. of Appl. Polym. Sci. 1994, 52, 545-548.
- [19] M. Kaneko, S. Kumagai, T. Nakamura, H. Sato, J. of Appl. Polym. Sci. 2004, 91, 2435-2442.
- [20] G. Gordon, B. R. Main, Polym. Degrad. & Stab. 1983, 5, 215-225.
- [21] Gordon, B. R. Main, Polym. Degrad. and Stab. 1985, 11, 9-25.
- [22] W. Hao, J. C. Shuang, Z. Jun, Col Polym. Sci. 2009, 287, 541-548.
- [23] S. Bag, V. P. Kumar, S. Maiti, J. of Appl. Polym. Sci. 1999, 71, 1041-1048.
- [24] C. Arribas, D. R. Rueda, Makromol Chem. 1991, 192, 491-497.
- [25] T. Susanne, K. Wolfgang, L. Thomas, Polym. Surface Modi: Relevance to Adhesion, 2007, 4, 157-170.
- [26] L. Xiaoying, S. Tan, N. Zhao, S. Yand, J. Xu, J. of Collo. and Interf. Sci. 2007, 311, 186-193.
- [27] K. J Less, E. G. Wilson, J of Phy C: Solid State Physics, 1973, 6, 3110.
- [28] M. Pascual, R. Balart, L. Shanchez, O. Fenollar, O. Calvo, J. of Mat. Sci. 2008, 43, 4901-4909.