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PII: S0014-3057(09)00067-6
DOI: 10.1016/j.eurpolymj.2009.02.011
Reference: EPJ 4957

To appear in: *European Polymer Journal*

Received Date: 5 March 2008
Revised Date: 7 January 2009
Accepted Date: 12 February 2009

Please cite this article as: Alves, P., Coelho, J.F.J., Haack, J., Rota, A., Bruinink, A., Gil, M.H., Surface modification and characterization of thermoplastic polyurethane, *European Polymer Journal* (2009), doi: 10.1016/j.eurpolymj.2009.02.011

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Surface modification and characterization of thermoplastic polyurethane

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Keywords: Thermoplastic polyurethane, surface coating, contact angle, thermal properties

Abstract

This work reports the modification of thermoplastic polyurethanes (TPUs) in order to enlarge their application range, for example, as biomaterials by increasing its hydrophilicity.

A TPU was successfully modified by using three different strategies: ultra-violet irradiation (UV), gamma irradiation (GI) and interfacial modification (IM). The results suggested the possibility of modifying the polyurethane-based surface either with

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poly(ethylene glycol) (PEG) or hydroxylethyl methacrylate (HEMA) or hexamethylene diamine (HMD) or chitosan (CT) by using any of these methods. The properties of the grafted PU were evaluated by surface, structural and thermal analysis. The results suggest that, among the methods studied in this work, the modification by gamma irradiation (GI) seems to be the most promising, since this method gives high values of grafting yield and has the advantage of providing a clean modification, meaning that no initiator is needed.

1 Introduction

The biological response to materials and devices is largely controlled by materials surface chemistry and structure. On this matter, the modification of polymeric surfaces is of outstanding importance aiming to develop materials that could maximise the materials performance in specific applications. Using such approach, it is possible to join the bulk properties of certain polymers by modifying only its surface [1]. Depending on the application, different properties may be desired.

Surface modification aims to tailor the surface characteristics of a material for a specific application without detrimentally affecting the bulk properties [2].

The surface properties that have utmost importance are the chemical structure (hydrophilicity and presence of groups that could initiate reaction in biological systems) and morphology (the distribution and abundance of hydrophilic/hydrophobic and crystalline/amorphous phases and surface topography) [3].

Materials can be surface modified by using either biological or chemical or physical methods. The surface modification can be carried out by radiation grafting of monomers [4,5], chemical modification, immobilizing biological molecules [6,7] and silanization

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[8]. With these techniques surfaces have been modified using molecules like poly(ethylene glycol) [1,9], sulfobetaine monomer [10], copolymer of warfarin [11], and other molecules containing hydroxyl groups [12,13].

In this work, a commercial pre-processed polyurethane was used as support for all the modifications. Elastollan®1180A50 (polyether-based thermoplastic polyurethane) was tested with the intent to be used as base material of a cell based biosensor. Thermoplastic polyurethanes (TPU) are currently used in several industrial branches in particular as coating, adhesives, engineering materials as well as films [14].

This material was chosen not only, due to its high mechanical flexibility, but also due to its properties (free from plasticizers, good heat resistance) and its ability to be processed by moulding. Elastollan®1180A50 exhibits excellent abrasion resistance, toughness, transparency, hydrolytic stability and fungus resistance [15].

The aim of this research work was to increase hydrophilicity of Elastollan 1180A50. It is known that cell adhesion increase by decreasing the water contact angle up to around 70º [16-19]. Maximal cell adhesion occurs on surfaces with moderated water contact angle. Although, on surfaces with higher or lower wettabilities, cell adhesion decrease [17]. Therefore, in this work the surface of Elastollan®1180A50 was modified either with PEG 6000 or HEMA or HMD or CT by using UV irradiation, GI and IM. The assessment of the modification yield, material performance and properties were done using different polymer characterization techniques: Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR), contact angle (CA) determinations, dynamic mechanical thermal analysis (DMA), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

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2 Experimental procedures

2.1 Materials and Methods

The Dibutyltin dilaurate 95%, 1,6-Diisocyanatohexane 98% (HDI), hexanethylenediamine (HMD), medium molecular weight chitosan (75-85% deacetylated) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Sigma-Aldrich. The isopropylthioxanthone (ITX) was ordered form Ward Blenkinsop & Co Ltd. Polyethylene glycol 6000 (PEG 6000) was purchased from Fluka. The solvents (methanol and toluene) were ordered from José Vaz Pereira, S.A, Portugal.

Elastollan®1180A50 was ordered from BASF. All chemicals were used as received.

The materials were modified in order to turn their surface cell repellent by means of the introduction of specific chemical groups such as hydroxyl or amino groups [20,21].

Figures 1 to 3 present the reactions related to the different surface modifications of the polyurethane-based materials.

Surface modification by grafting with PEG 6000 (or HMD)

The surface modification by grafting was done in a two-step procedure similar to the one described by Tan et al. [9] and Yuan et al. [10]. Both steps were carried out under nitrogen atmosphere, using toluene as solvent (and swelling agent) and dibutyltin dilaurate 95% as the catalyst. In the first step, the polyurethanes were functionalized with HDI. A TPU sample (10g) was immersed into 100mL toluene containing 5% (v/v) HDI and 0.25% (v/v) Dibutyltin dilaurate 95%, for 1h at 70ºC. Then, the TPU sample was washed with toluene. In the second step PEG 6000 (or HMD) was grafted onto the TPU surface by letting the hydroxyl groups react with the isocyanate end groups of HDI. A 10% (w/v) of PEG 6000 (or HMD) solution in toluene was added to the TPU

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sample after the first step and left to react for 24h at 45ºC and washed with toluene, in order to remove all the unreacted monomer. The sample was finally dried in a vacuum oven at 35ºC until constant weight.

Surface grafting with chitosan

This modification was also performed in a two-step procedure. The first step was the same described in the previous modification with PEG 6000 (or HMD). However, in the second step, the functionalized polyurethane samples were immersed in a chitosan solution (1%) for 5h at 45ºC. The sample was taken out from the chitosan solution, washed with distilled water and dried in a vacuum oven at 35ºC. Figure 1 illustrates the two steps reaction carried out with PEG6000, HMD and chitosan.

< Insert Figure 1 >

Surface modification by gamma irradiation with HEMA

Here, 20 g of Elastollan sample were dispersed in 30mL of 15% (v/v) HEMA solution in methanol (MeOH). The samples were then irradiated with a ^{60}Co source at dose-rate of 0.3 kGy h^{-1} for 21 hours at room temperature. After irradiation the samples were rinsed and extracted (in a soxhlet) with MeOH and dried in a vacuum oven at 35ºC until constant weight. Figure 2 shows the simplified scheme of the GI mechanism. Here, HEMA was grafted into the TPU's surface without using any chemical compounds.

< Insert Figure 2 >

Grafting of PHEMA onto polyurethane surface by UV irradiation

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In an Erlenmeyer flask were introduced 10g of TPU, 1ml of HEMA, 50mL of toluene and 100mg of ITX. The solution was irradiated during 90 minutes with an UV light (Mineralight® Lamp, Model UVGL-48) at 60ºC. Finally the samples were immersed in water for 1 day and dried in a vacuum oven at 35ºC. UV irradiation with HEMA modification is represented in Figure 3. In this modification a photosensitizer (ITX) was used to induce necessary radicals for grafting process.

< Insert Figure 3 >

3 Characterization techniques

The grafting yield (GY) was determined by calculating the percentage increase in weight as described in Equation (1), where W_0 and W_g represent the weights of the initial and grafted polymer, respectively. The samples were weighted in an analytical balance.

$$GY(\%) = \frac{W_g - W_0}{W_0} \qquad (1)$$

Water contact angle as well as surface free energy of plane materials surfaces was performed at room temperature in an OCA 20 from Dataphysics. Water contact angle of the samples were evaluated by static contact angle measurements using the sessile drop method. Surface free energy was obtained according the Owens-Wendt-Rabel and Kaelbe method (OWRK) [22] by static contact angle measurements with four liquids: water, ethylene glycol, propylene glycol and formamide.

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FTIR spectra were obtained in a Nicolet 750, using a Golden Gate ATR accessory from Specac, where the products were analysed as prepared. Resolution was 4 and the number of scans 64. Dynamical Mechanical Thermal Analysis (DMA) of thick specimens (15.20 mm x 7.45mm x 1.2 mm) were performed by a Triton Tritec 2000 in the Constrain Layer Damping mode at 2 frequencies (1Hz and 10Hz), using cryogenic nitrogen, with a standard heating rate of 2ºCmin^{-1}. The Tg was determined as the peak of tan δ (Tan δ =E''/E') where E'' and E' are the loss and storage modulus, respectively. The TGA curves were determined, in the temperature range 20-600ºC, using a heating rate of 10ºCmin^{-1}, under a dry nitrogen atmosphere with a flow-rate of 100.0mlmin^{-1}, in a SDT Q600 from Thermal Analysis.

The material's surface was observed by SEM, before and after coating. The samples were sputter coated with a thin layer of gold, under argon atmosphere and examined at room temperature, in a JSM-5310 (JEOL, Japan) scanning microscope operating at 20 and 25 kV.

4 Results and discussion

The TPU material was selected, as mentioned before, considering its properties and mainly because of its ability to be processed by injection moulding.

4.1 Grafting Yield

The grafting yield was used to measure the effectiveness of the synthesis methods studied in this work. The theoretical yield is typically calculated assuming that the

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stechiometric amount of the reactant is converted into product and it can be isolated in pure form.

The results presented in Table 1 show that, in terms of efficiency, the modifications by GI and interfacial modification with HMD were the better methods, being the higher yield obtained with the GI process.

< Insert Table 1 >

4.2 Attenuated total reflectance infrared spectra (ATR-FTIR)

As reported in the literature, the hard segments of TPU contains NH and C=O groups. These structures can interact and form intermolecular hydrogen bonding [23,24]. Thus, NH (3500–3000 cm^{-1}) and C=O (1800–1640 cm^{-1}) stretching vibration absorption regions are very important infrared regions. Both the NH and C=O absorption peaks contributes to the overlapping bands of their free and hydrogen-bonded group, respectively.

The unmodified TPU (Figures 4a) was characterized by a peak at around 3325 cm^{-1} due to the absorption of N–H stretching vibration. Two peaks of carbonyl absorption can also be identified, which can be due to a free carbonyl stretching vibration at 1710 cm^{-1} and a hydrogen-bonded at 1730 cm^{-1}.

The FTIR spectra of the TPU material are affected by the surface modification depending on the method used (Figure 4).

In all modifications no shift of absorption peaks of N–H group was seen, as the absorption bands of N–H group were sensitive toward hydrogen bond formation, only differences in the amount of NH groups can be observed. A similar behaviour was

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observed with the C=O peaks. No shift of the peak was found, however a decrease can be observed in the relative concentrations of free and hydrogen-bonded carbonyl group after each modification.

< Insert Figure 4 around here >

From the spectra in the Figure 4, a band appears at 2250 cm^{-1} in the (b) trace that was not present on the unmodified membrane – (a) trace. This result suggests that the membranes were successfully functionalized with isocyanate groups. In the second step of the reaction (traces (c), (d) and (e)) this peak disappears, meaning that the modification was effectively achieved once the isocyanate groups reacted with the other compounds (either PEG 6000 or HMD or CT). The modification with PEG 6000 reveals a spectra with a slightly broad band at approximately 3500 cm^{-1}, which indicates the presence of hydroxyl groups. In the GI (Figures 4f) and UV irradiation (Figures 4g), a slight band around 3500 cm^{-1} can be seen, which indicates the presence of the HEMA's hydroxyl groups. UV irradiation also shows a significant decrease of the peaks intensity, meaning a decrease of the NH groups.

The FTIR analysis indicates the success of the grafting copolymerization based on the presence of the characteristic peaks expected for the compounds used in the grafting polymerization.

4.3 Contact angle and surface free energy

The contact or wetting angle is most often assessed by placing a small liquid droplet on a flat horizontal solid surface. The contact angle is the angle which is formed by the

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baseline and the tangent to the drop contour at the three phase point. This value is specific for any given system being determined by the interactions of the three interfaces. If a liquid is in contact with a plane solid surface, three interfacial free energies have to be assumed and, the equilibrium of forces at the edge of a resting drop can be described by Young's equation (Eq. 2):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\theta) \qquad (2)$$

In Equation (2), γ_{SV}, γ_{SL} and γ_{LV} represent the interfacial tension of the solid/vapour, solid/liquid and liquid/vapour interfaces, respectively. θ represents the equilibrium contact angle [25,26].

Owens-Wendt- Rabel and Kaelbe distinguish, for the first time, between disperse and polar interactions. Polar interactions contain Coulomb interactions between permanent dipoles and the ones between permanent and induced dipoles. Disperse interactions are caused by time fluctuations of the charge distribution within the molecules [22].

In the present work, the contact angles were measured of the different polyurethanes used and the resulting materials after modification using four liquids: water, ethylene glycol, propylene glycol and formamide. Table 2 shows the water contact angle results.

< Insert Table 2 >

The presence of polar functional groups such as OH groups or NH_2 groups increases the hydrogen bounding interactions [27] and therefore the contact angle decreases.

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Hydrophilic surfaces with strongly-bound water interface are related to low proteins adsorption. However, this is not a general rule. Proteins can be adsorbed near the surface in a manner that does not require dehydration of the surface [28].

Generally, the contact angle decreases when different modifications were carried out (Table 2). The water contact angle decreases significantly for the modification with PEG 6000. This result can be ascribed to the higher amount of hydroxyl groups relatively to the other compounds, which leads to an increase in hydrophylicity. This fact is also observed by the results obtained for the surface energy (Table 2), which were determined according to Owens-Wendt-Rabel and Kaelbe method (OWRK) using the obtained contact angles as shown in Table 2.

The increase of surface energy can be explained by the introduction of polar functional groups. Variations in contact angle can be not only due to differences in surface chemical composition, but also due to differences in surface structure [29].

4.4 Scanning electron microscope (SEM)

To analyse surface (sub-)microstructure of the starting TPUs-based materials and the modified ones, the different samples were analysed by SEM.

Figure 5 shows SEM pictures of the material's surfaces after each modification. Each modification resulted in uniform surfaces with different surface topography. The smoothest surfaces were obtained by UV curing with HEMA (Figure 5e). Interfacial modification with PEG 6000 (Figure 5b) also induced smooth surfaces.

As illustrated by Figure 5c and 5d after coating by interfacial modification with HMD and by Chitosan, respectively, the surfaces are rougher than the unmodified materials.

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< Insert Figure 5 >

4.5 Thermal Analysis

The Dynamical Mechanical Analysis (DMA) is one of the main techniques to study the mechanical and thermal properties of the polymers, due to its high sensitivity to different molecular events. DMA traces allow the determination of the temperature transitions and miscibility issues of the polymeric materials. DMA analysis was performed by using stainless steel pockets to support the material in the DMA and to enable a turning and heating of the samples until melting without destroying the sample geometry or contaminating the instrument.

Thermal characterization of segmented polyurethanes has been carried out by several researchers [30,31] indicating the presence of multiple transitions in these materials. This behaviour is due to a specific phenomenon in each phase of the segments that form the TPU. In the present study the Tan δ curves obtained from the DMA technique for the starting TPU and the grafted TPU were assessed partly in the multifrequency mode (Figure 6).

< Insert Figure 6 >

Maximal values of the damping factor, Tan δ, of the pure Elastollan®1180A50 (Figure 6) were obtained at -34ºC at 1 Hz. The sensitivity of peak to the frequency indicates the present of the α transition (glass transition; Tg). This relaxation peak is attributed to the soft segment transition from the glassy to the viscoelastic state. The Tg value achieved in the present work is close to the values reported by other authors that used similar

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polyurethane materials [14,30]. The melting point (T_m) of the phase of the TPU containing the hard segments can be observed at 110ºC. The region between the Tg and the Tm corresponds to the range of work temperatures expected for these materials.

Figure 7 shows the damping factor obtained for each modification.

< Insert Figure 7 >

Figure 7 suggests the presence of two peaks in the region of glass transition (-57 and -34ºC), which indicates a certain degree of immiscibility of the various TPU components. It is known that the soft segment of the polyurethane can be used as an indication of the phase separation, since for materials well phase-separated the Tg will lie very close to the Tg of the soft segment. In this case, the composition of the TPU material is still undisclosed by the producing company. Because of that it is not possible to confirm the proposed explanation. It is interesting to notice that first peak remained regardless the modification done.

The modification of Elastollan®1180A50 with PEG6000 resulted in a shift of the Tg from -34 ºC to -40ºC making the graft polyurethane more flexible. It is also possible to observe a peak that starts at 40ºC corresponding to the melting point of PEG6000. On the other hand, the grafting with HEMA by UV and by GI conduct to a smaller Tg shift (-33ºC and -40ºC, respectively). The different graft copolymerizations with the materials used in this work reveals small changes of Tg compared to the pure polyurethane. This result could be expected due to the grafting yields observed (Table1).

The influence in the thermal stability of the methods and materials grafted onto the TPU studied in this work was also assessed by thermogravimetry.

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< Insert Figure 8 >

The thermogravimetric curves of Elastollan®1180A50 and its modifications are shown in Figure 8. The curves presented consist of three stages. Some parameters, such as temperature of maximum degradation of each step (T_i in ºC) were determined considering the derivative curves. The percentage of mass loss in each stage of degradation (M_i in %) and residue at 600ºC (the end temperature of the analysis) for each modification are shown in Table 3.

< Insert Table 3 >

The first stage is apparently associated with the adsorbed water, where a small percentage of mass loss. The other two different stages of degradation are very similar in both modified and unmodified materials. The second stage, around 350ºC, can be attributed to the decomposition of the TPU's hard segment. Finally, the third stage, around 420ºC corresponds to the effective degradation of the polyurethane, with a higher percentage of mass loss. It is interesting to notice that a very similar degradation pattern is observed for both pure and modified polyurethane, indicating that the bulk structure was not affected by the modification. The TPUs grafted with HEMA by GI starts the first mass loss around 60ºC and ending at 220ºC. Due to the low percentage of mass lost (about 10%) at this temperature range and the low onset temperature it is difficult to ascribe this behaviour to any degradation phenomena. Furthermore, the degradation profile above 220ºC is quite similar to the one observed for the pure TPU.

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5 Conclusions

The obtained results suggest that it is possible to modify the surfaces by using ultra-violet irradiation (UV), gamma irradiation (GI) and interfacial modification (IM) either with poly(ethylene glycol) (PEG) or hydroxyl ethyl methacrylate (HEMA) or hexamethylene diamine (HMD) or chitosan (CT).

ATR–FTIR and SEM characterizations confirmed the graft polymerization on the TPU surfaces. Surface hydrophilicity of the TPU membrane was enhanced by the grafting of an hydrophilic PEG layer.

All of the modifications induced an increase of hydrophilicity and higher thermal stability, which the glass transition temperature was nearly unaffected.

Considering the different modifications, GI seems to be the most efficient one. Because it leads to a higher grafting yield and hydrophilicity was slightly improved. Nevertheless, according to some authors [16-19] this extends of surface modification is not enough to promote cell adhesion. Apart from that, GI is also a simple technique with sterilization properties. Although, the results presented in this work suggest that IM with PEG is the better modification. Looking at the water contact angle results, with this chemistry, better cell adhesion would be expected. Apart from that, this modification is also slightly more thermal stable.

6 Acknowledgements

The present study was supported by the European Commission through the specific targeted research project CellForce of the 6th FP (Contract N°: NMP4-CT-2005-016626).

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8 Figure Captions

Figure 1 – Two step reaction mechanisms.

Figure 2 – Gamma irradiation mechanism.

Figure 3 – UV irradiation mechanism.

Figure 4 – Elastollan®1180A50 FTIR spectra, were: (a) unmodified, (b) funcionalization with HDI, (c) IM with PEG 6000, (d) IM with HMD, (e) IM with Chitosan, (f) HEMA by GI, (g) HEMA by UV.

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Figure 5 – SEM pictures of Elastollan®1180A50 (a) unmodified, (b) IM with PEG 6000, (c) IM with HMD, (d) IM with Chitosan, (e) HEMA by UV, (f) HEMA by GI.

Figure 6 – Plots of tan δ versus temperature for the pure Elastollan®1180A50 assessed at two different frequencies.

Figure 7 – Plots of tan d versus temperature for the pure Elastollan®1180A50 and grafted copolymers as measured at 1Hz.

Figure 8 – Termogravimetric curves of the Elastollan®1180A50 the graft-copolymers prepared from the pure PU (a) unmodified, (b) IM with PEG 6000, (c) IM with HMD, (d) IM with Chitosan, (e) HEMA by UV, (f) HEMA by gamma irradiation.

9 Table Caption

Table 1 – Yield of grafting yield of the various samples. Mean values ± S.E.M. of 3 independent experiments are shown.

Table 2 – Effects of material surface modification on Water contact angle and surface tension (nN/m). Mean values ± S.E.M. of 3 independent experiments are shown.

Table 3 – Thermogravimetric parameters for the studied material and its surface modifications.

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Table 3

	Yield (%)
Interfacial modification with PEG 6000	9.17 ± 0.092
UV Curing with HEMA	7.38 ± 0.137
Interfacial modification with HMD	12.23 ± 0.165
Gamma irradiation with HEMA	13.45 ± 0.124
Interfacial modification with Chitosan	8.88 ± 0.130

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Table 2

	Contact angle (°)	Surface tension (nN/m)
Unmodified	99.6 ± 1.2	20.53 ± 4.00
Interfacial modification with PEG 6000	72.1 ± 0.8	32.46 ± 1.98
UV Curing with HEMA	92.0 ± 1.7	23.26 ± 2.26
Interfacial modification with HMD	79.7 ± 2.1	22.95 ± 2.78
Gamma irradiation with HEMA	86.2 ± 1.5	22.76 ± 2.12
Interfacial modification with Chitosan	90.6 ± 1.3	19.96 ± 1.48

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Table 3

	Stage 1		Stage 2		Stage 3		Residue at 600ºC (%)
	T_1	M_1	T_2	M_2	T_i	M_3	
Unmodified	254.0	1.35	364.7	31.55	418.1	68.34	4.2
Interfacial modification with PEG 6000	219.1	2.32	358.9	30.92	420.8	66.75	7.0
UV Curing with HEMA	289.9	1.82	363.5	32.49	415.0	69.68	3.8
Interfacial modification with HMD	--	--	349.1	28.04	418.8	67.34	6.2
Gamma irradiation with HEMA	125.0	2.67	371.8	34.40	417.7	66.21	4.7
Interfacial modification with Chitosan	252.4	1.81	356.1	31.68	420.0	68.00	6.2

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Figure 1.

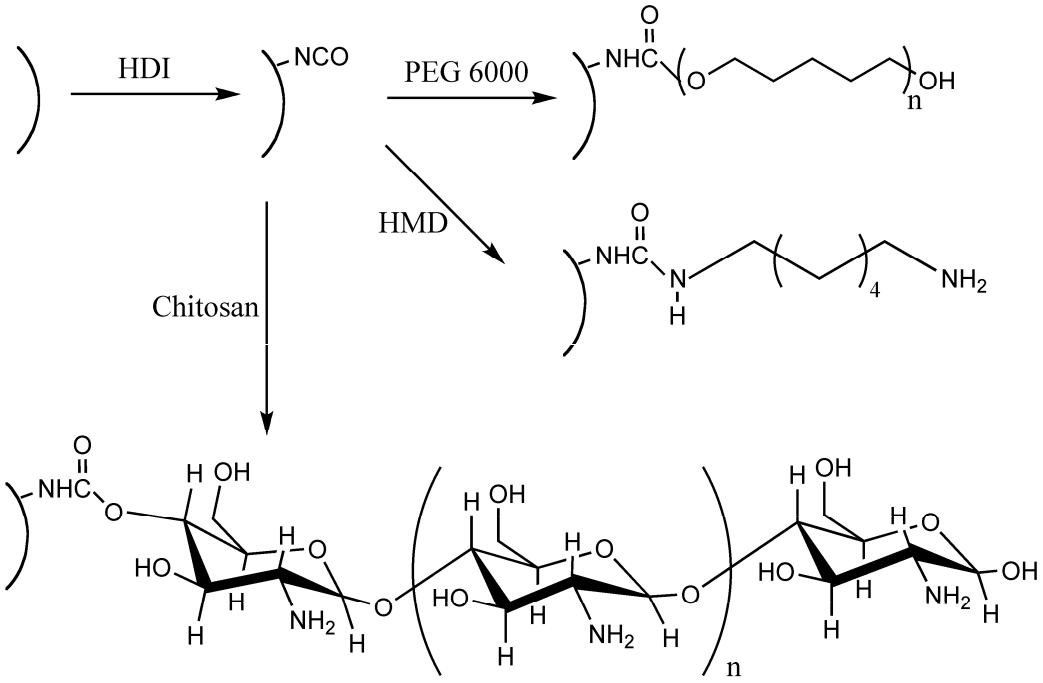

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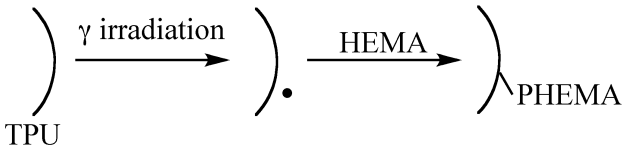
Figure 2.



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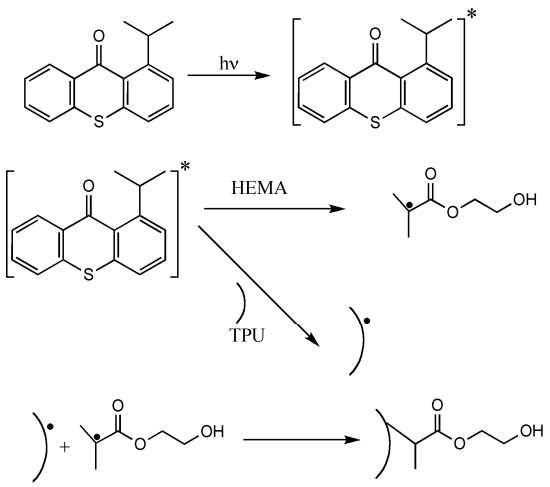

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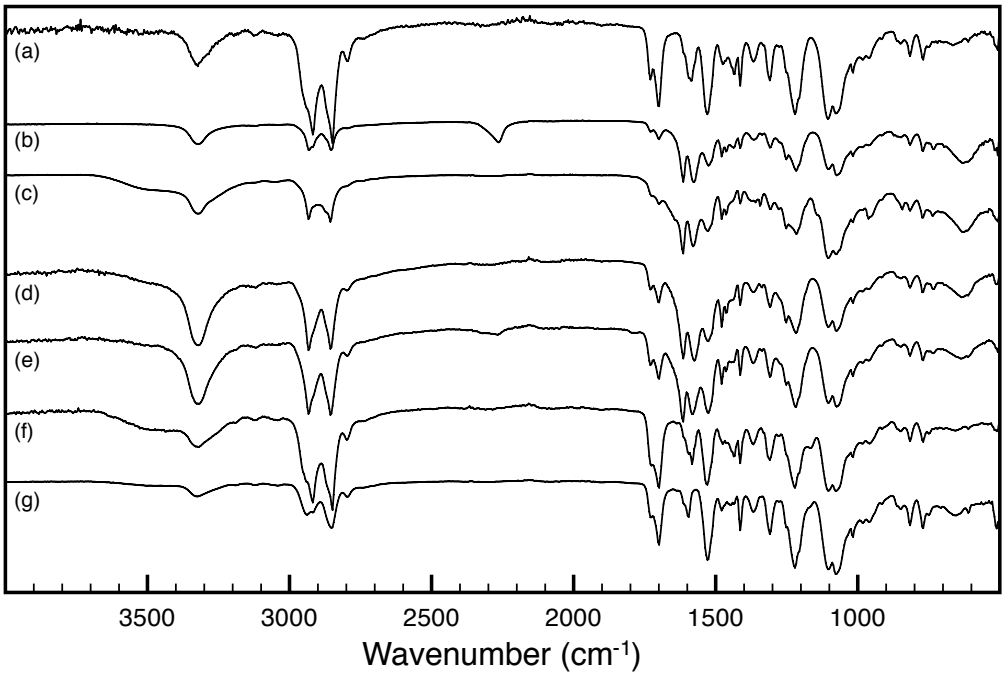

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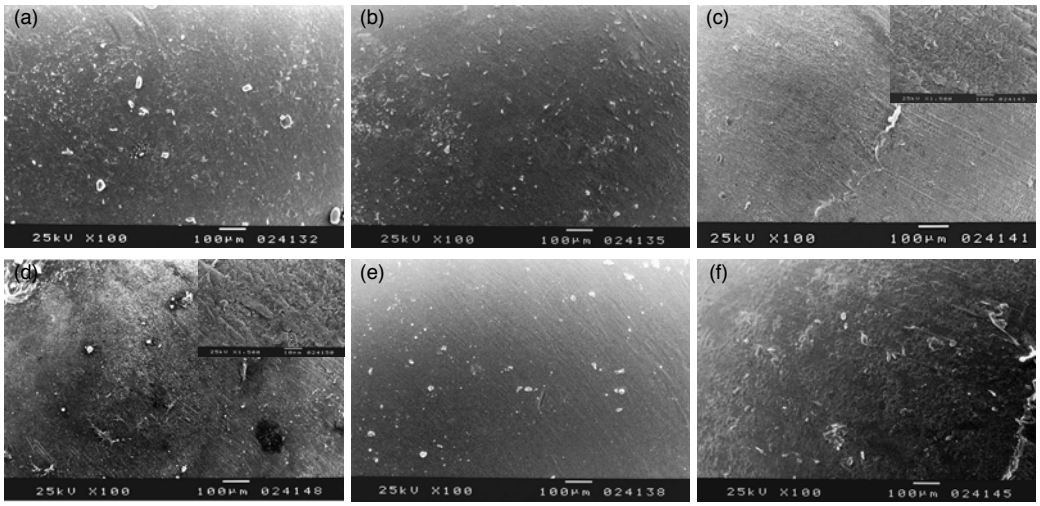

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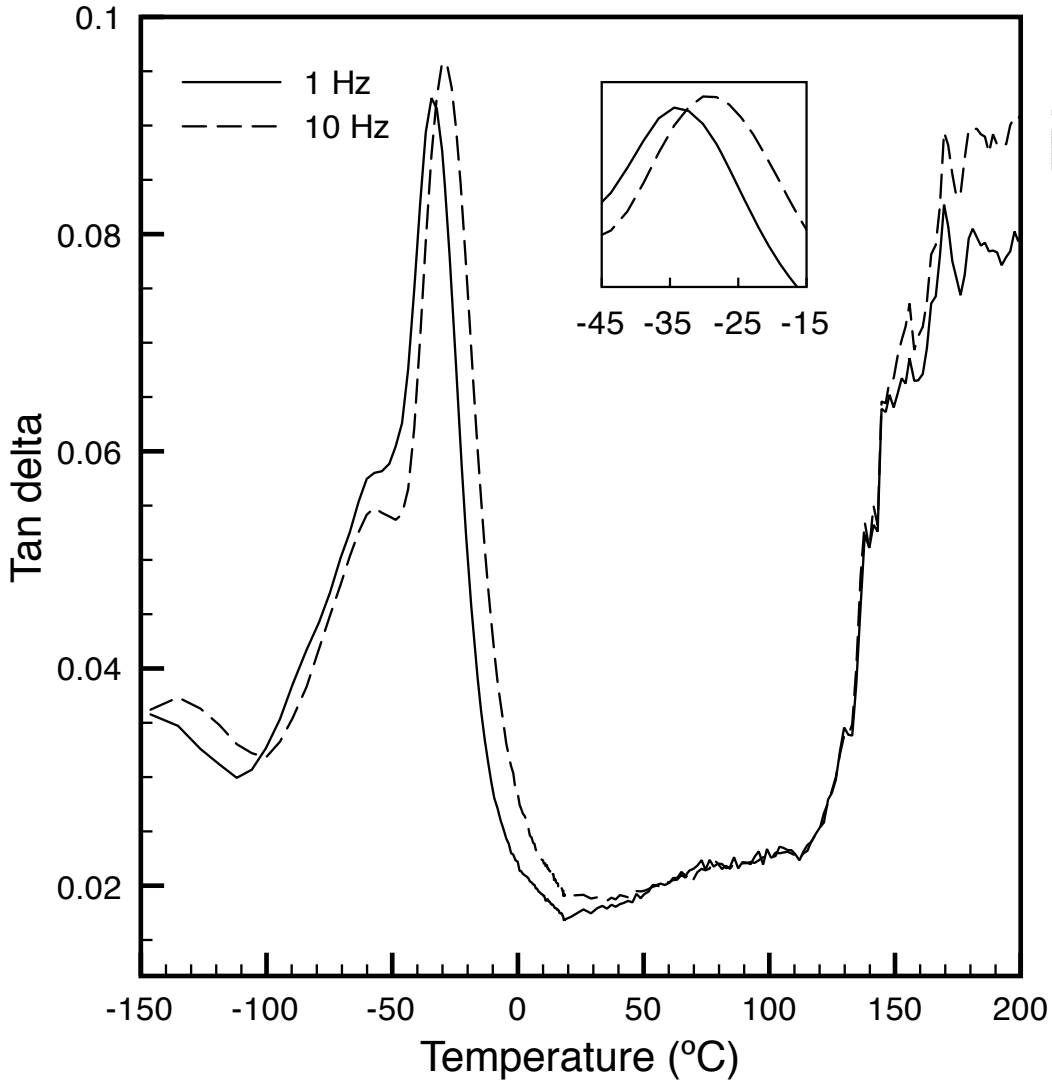

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Figure 7.

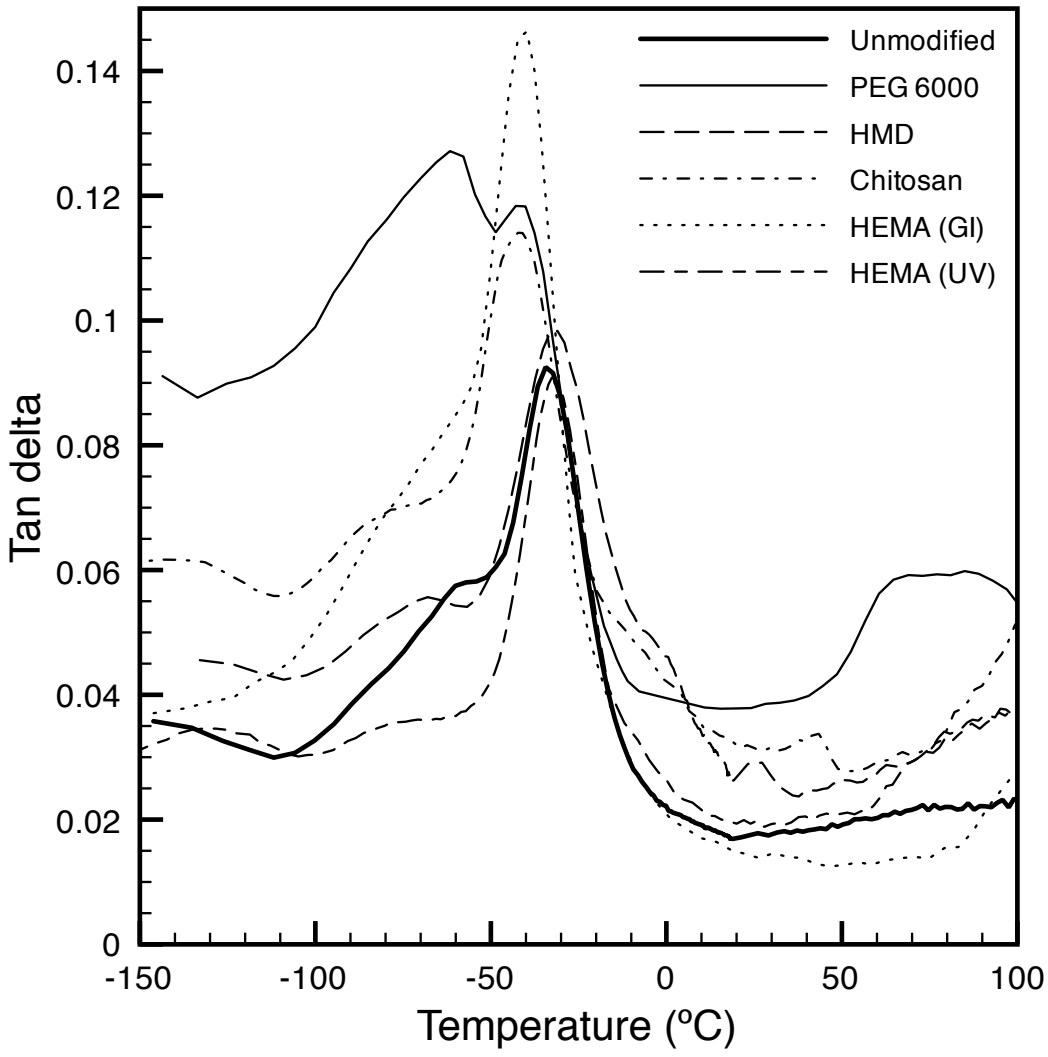

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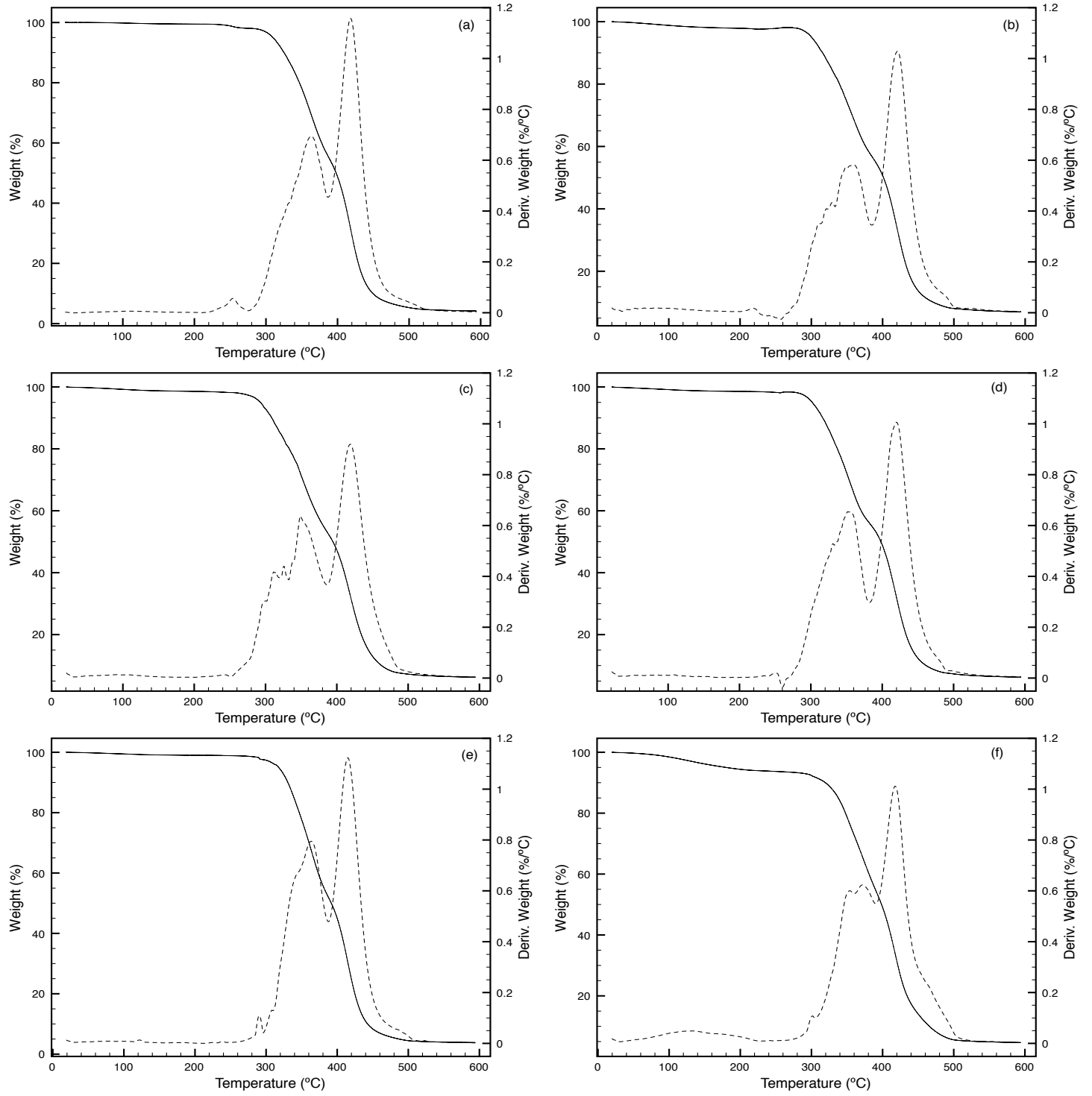
Figure 8.

ACCEPTED MANUSCRIPT


(a)
(b)
(c)
(d)
(e)
(f)
Weight (%)
Deriv. Weight (%/ºC)
Temperature (ºC)
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20
40
60
80
100
0
0.2
0.4
0.6
0.8
1
1.2
100
200
300
400
500
600