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The effect of sulfonation level and molecular weight on the tensile properties of polyoxadiazoles

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ABSTRACT: The tensile properties of sulfonated polyoxadiazoles have been studied as a function of molecular weight and sulfonation level. All sulfonated polyoxadiazoles synthesized through a polycondensation reaction of the hydrazine sulphate salt and a dicarboxylic acid in poly(phosphoric acid) exhibit rigid-ductile behavior with high Young's modulus (3-4 GPa) and with larger elongations at break (up to 120%). Sulfonated polyoxadiazoles with maximum reproducible tensile strength (190 ± 6.9 MPa) could be synthesized in the frame of time of 4-5 h.

Keywords: polyoxadiazole; molecular weight; tensile properties

1. Introduction

In recent years, high temperature resistant engineering polymers have gained acceptance for use as matrices in advanced polymer composites for aerospace structural applications, including military aircraft and missiles [1-2]. Recent applications of reinforced polymers in aircraft propulsion systems have resulted in substantial reductions in both engine weight and manufacturing costs. Unfortunately, the low thermal-oxidation stability of these materials severely limits the extent of their application. Poly(1,3,4-oxadiazole)s have been the focus of considerable interest with regard to the production of high-performance materials, particularly owing to their high thermal stability [1]. Besides their excellent resistance to high

temperature, polyoxadiazoles present a combination of properties (such as mechanical strength, thermal and chemical stability) that makes them good candidates for application as high temperature fibers [3], reinforcement materials [4] and membrane materials [5,6].

Synthesis of polymers containing oxadiazole rings was part of a NASA program on high performance/high temperature polymer for potential use as coatings and composite matrices on aerospace vehicles [7,8]. Connell et al. [8], have synthesized poly(1,3,4-oxadiazoles) by aromatic nucleophilic displacement reaction of dihydroxyphenyl monomers with aromatic dihalides or aromatic dinitro compounds. The polymerizations were carried out in polar aprotic solvents such as sulfolane or diphenylsulfone using alkali metal bases such as potassium carbonate at elevated temperatures. The copolymers containing oxadiazole rings exhibiting respectively tensile strengths, modulus and elongations up to 100 MPa, 3 GPa and 4%. Gomes et al. [6,9,10] have performed a systematic study on the influence of distinct synthesis parameters, when polymerizations are performed in poly(phosphoric acid) on the final properties of polyoxadiazoles, e.g. molecular weight, residual hydrazide groups and sulfonation level. However, up to know no correlation between synthesis parameters and tensile properties of sulfonated polyoxadiazoles has been provided. Sulfonated polymers may show improved properties such as better wettability, higher antifouling capacity, higher solubility in solvents for processing, higher gas permeation properties, higher proton conductivities and presence of active functional groups to improve compatibility with fillers. However, depending on the sulfonation conditions, degradation of polymer can occur resulting in a decrease of the molecular weight and as a consequence a decrease of mechanical properties.

In this study, the effect of the reaction time on the molecular weight, thermal stability and tensile properties of sulfonated poly(4,4'-diphenylether-1,3,4-oxadiazoles) was for the first time analyzed. Sulfonated polyoxadiazoles with excellent and reproducible tensile properties (tensile strength up to 200 MPa, elastic modulus around 4 GPa and elongation at break in the range 40-60%) could be synthesized through a polycondensation reaction of the hydrazine sulphate salt and an aromatic dicarboxylic acid in poly(phosphoric acid) in the frame of time of 4-5 h. The tensile properties of the sulfonated polyoxadiazole films obtained in this study, confirms the classification of this polymer as high performance polymers with great potential for engineering applications.

2. Experimental Section

2.1. Materials

Dicarboxylic acid 4,4'-diphenylether, DPE (99%, Aldrich), Dimethyl sulfoxide, DMSO (>99%, Aldrich), hydrazine sulfate, HS (>99%, Aldrich), sodium hydroxide, NaOH (99%, Vetec), poly(phosphoric acid), PPA (115% H₃PO₄, Aldrich). All chemicals were used as received.

2.2. Synthesis of sulfonated poly(diphenylether-1,3,4-oxadiazole) s

The synthesis condition has been selected considering previously reported synthesis method for sulfonated polyoxadiazoles with high molecular weight [6,9,10]. Hydrazine sulfate salt, HS, and dicarboxylic diacid 4,4'-diphenylether, DPE were reacted at 160°C in polyphosphoric acid, PPA, under dry nitrogen atmosphere for 2-7 h. Fig. 1 shows a scheme of the reaction synthesis. The molar dilution rate (PPA/HS) and the molar monomer rate (HS/DPE) were kept constants and equal to 10 and 1.2, respectively. Afterwards, the reaction medium was poured into water containing 5% w/v of sodium hydroxide (99%, Vetec), for precipitation of the polymer. The final reaction medium is very viscous, which makes precipitation and neutralization of the polymer very difficult. Thus, the final polymer may present high amounts of residual solvent, which may cause degradation. To avoid this, the polymer sample was shredded into small fragments using a Retsch Grindomix GM 200 Knife Mill. The reaction medium is first poured into water containing 5% w/v of sodium hydroxide. Then, the polymer suspension feeds a shredder, where the polymer material is shredded into small fragments. The suspension containing the shredded material was finally transferred to a container, where purification proceeds. The purification comprises first the neutralization of the pH of the suspension, change of the water of suspension which was kept at pH 7 for 18h, agitation of the suspension for more 3h. The pH of this polymer suspension was controlled according to literature [10]. Figure 2 illustrates the aspect of the final polymer suspension and shows the polymer samples before and after of the shredder.

2.3. Polymer Characterization

The polymer structures were characterized by elemental analysis conducted on a Carlo Erba Elemental Analyzer-Mod 1108. A Viscotek SEC apparatus equipped with SEC 10.000 Eurogel and PSS Gram 100, 1000 columns, with serial numbers HC286 and 1515161 and size 8 x 300 mm was employed to evaluate the weight average molecular weights of the polymer samples. The equipment was calibrated using polystyrene standards (Merck) with weight

average molecular weights ranging from 309 to 944,000 g/mol. A solution with 0.05 M lithium bromide in DMAc was used as carrier.

2.4. Film preparation

Homogeneous films were cast from solutions with a polymer concentration of 2.8 wt. % in DMSO. After casting, the DMSO was evaporated in a vacuum oven at 60°C for 24h. For further residual solvent removal, the membranes were immersed in water bath at 60°C for 48h and dried in a vacuum oven at 60°C for 24h. The final thickness of the films was about 60 μm .

2.5. Thermal and mechanical analysis

Thermogravimetric analysis (TGA) experiment was carried out in a Netzsch 209 TG, equipped with a TASC 414/3 thermal analysis controller. The film sample, under nitrogen atmosphere, was heated from 100 to 500°C at 10°C/min. Dynamic mechanical thermal analysis (DMTA) was used for determination of glass transition temperature (T_g), storage modulus (E') and loss tangent ($\tan \delta$). DMTA was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1Hz and at an initial static force of 0.1 N. The temperature was varied from 25 to 500 °C at a heating rate of 2°C/min and at a constant strain of 0.05%. Tensile testes were performed according to the ASTM D882- 00 using a Zwick-Roell equipment with a 500 N load cell operating at cross-head speeds of 25 mm min⁻¹. The reported values correspond to an average of ten specimens of at least two different films.

3. Results and Discussion

The thermal stability of all sulfonated polyoxadiazoles was confirmed by TGA as shown in Table 1. All SPOD-DPE show 5% weight loss in the range of 463-470°C and the residue at 500°C was in the range of 79-81%. Increase of thermal and mechanical properties with reaction time has been observed. High storage modulus values in the range 2-3 GPa at 300 °C have been obtained. The analysis of Table 1 also indicates that sulfonation level and molecular weight simultaneously increase with reaction time. Sulfonation of polyoxadiazoles synthesized in poly(phosphoric acid) occurs by the presence of sulfuric acid in the solution of hydrazine sulfate salt ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$). This reaction involves an eletrophilic substitution reaction of the eletrophilic agent (SO_3) coming from the sulfuric acid and is activated by electron donating groups, in this case the ether group attached to the aromatic ring. Electron-

deficient group considerably reduces the reactivity of this electrophilic substitution reaction in the aromatic ring taking into account that the oxadiazole ring is an electron-withdrawing group. Gomes et al. [11] have shown that the sulfonation level of polyoxadiazoles containing electron donating groups synthesized in poly(phosphoric acid) increases with reaction time and is activated at temperatures higher than 150°C. An advantage of the sulfonated polyoxadiazole samples prepared by this direct method is that they have much higher molecular weights when compared to sulfonated samples prepared by post-sulfonation routes [6].

Figure 3 shows the average mass molecular weights (M_w) as a function of the reaction time. High molecular weights in the order of 10^5 g/mol were confirmed by SEC and simultaneously with lower polydispersity (around 2) were obtained by increasing the reaction time, as shown by the insert SEC profiles relative to polystyrene standard. The high molecular weight obtained for the sulfonated polyoxadiazoles can be attributed to the formation of three-dimensional cross linked structures [9]. The low polydispersity obtained in this study compared to the previous one [6] is essentially attributed to the shredding and neutralization of the polymer suspension, which has been shown to be fundamental steps to guarantee the total removal of residual PPA solvent in the polymer and consequently to avoid undesired degradation.

The analysis of Fig. 3 indicates that unimodal molecular weight distribution can be indeed obtained for reactions performed in the range of 4-6h, when polymer is shredded. Increasing further the time to 7h, also with shredding unavoidable species with lower molecular weights in the order of magnitude of 10^3 g/mol started to be formed due to the simultaneous degradation reaction [9]. The low polycondensation reaction time of 3h also leads to sample heterogeneity which can be attributed to the higher reaction medium viscosity compared to the other conditions. The reaction medium viscosity should depend on two competitive effects: 1) increase of reaction medium viscosity because of crosslinking linkages formation and polymerization reaction; 2) decrease of reaction medium viscosity because of sulfonation and degradation reactions [6,9,10]. Further increase of time to 4 h results in better homogeneity probably because of the three-dimensional crosslinked linkages starts to break resulting in lower viscosity and improved micromixing effects [10].

Exogenous effects during synthesis induced by small changes of mixing of the reaction medium as well as the monomer and solvent purity may have significant influence on molecular weight of polymer samples [9] as a consequence sulfonated polyoxadiazoles with lower molecular weights can be obtained. The main sources of fluctuation of the average

molecular weight are the high viscosity of the reaction medium, degradation reactions caused by the acid solvent, and the occurrence of secondary reactions (non-linear cyclodehydration reaction and crosslinking reaction) which compete with the linear cyclodehydration reaction of polyhydrazide into POD. These reactions are schematically presented in Figure 4.

The tensile properties of polymer samples are directly affected by the molecular weight values. Figure 5 shows the tensile strength values as a function of molecular weight. For the same polydispersity, as high the molecular weight as high the tensile strength. Similar trend has been observed by a NASA group when tensile strength is plotted as a function of polyimide molecular weights [12]. Additional factor is the sulfonation level which influences the dipole-dipole interaction between the sulfonated groups and as a consequence the T_g and mechanical properties. For similar molecular weights and polydispersity, the sample with higher sulfonation level (insert in Figure 5) shows the higher tensile strength, once the introduction of sulfonic acid groups increases the intermolecular interaction [13].

Figure 6 (a) shows representative stress-strain curves for the different reaction times. Average values for Young's modulus, E , tensile strength, σ_M and elongation at break, ε , as a function of reaction time (b) are given in Figure 6 (b). As it can be seen, all sulfonated polyoxadiazoles exhibits rigid-ductile behavior with high Young's modulus, E (3-4 GPa) and with larger ultimate elongations, ε (up to 120%). The analysis of Figure 6 indicates that sulfonated polyoxadiazoles with excellent and reproducible tensile properties can be synthesized in the frame of time of 4-5 h. With a reaction time of 3h, sulfonated polyoxadiazoles with very high tensile strength up to 250 MPa could be obtained. However, under this condition lower reproducibility of results was observed. The insert in Fig. 6 (a) shows representative stress-strain curves for the reaction time of 3h. The discrepancy observed in this condition may be attributed to the higher average molecular weight variation. The higher elongation at break for polymer samples synthesized at 3 and 7 h is explained by the presence of species with lower molecular weights in the order of magnitude of 10^3 g/mol (insert Figure 3), which may act as plasticizers, increasing polymer segmental mobility.

An additional factor affecting the elongation at break of samples could be the water uptake of the sulfonated samples after exposing them to the atmospheric moisture. Gomes et al. [6] have shown both by qualitative and quantitative measurements that water uptake increases for these sulfonated polymers with the increases of sulfonation level. In the present work, the higher elongations obtained for the sulfonated polyoxadiazole synthesized for 3h can be neither explained by the sulfonation level ($SL = 34$) nor by the water uptake at room temperature (19% at 100% relative humidity [6]), for instance when compared with the

samples synthesized for 4h (SL= 46 and water uptake=22% [6]) and 5h (SL= 50 and water uptake=25% [6]). Based on these results, it should be expected that species with low molecular weights play an important role as plasticizer for the polymers synthesized for 3-5h. Nevertheless, for the sample synthesized for 7h, absorbed water acting as plasticizer could also explain the high elongations obtained in this condition. The literature has shown that sulfonated polymers show lower elongation at break than the non sulfonated ones [14,15]. The changes in the mechanical properties may be most ascribed to the lower final polymer molecular weight after functionalization. When changes in the molecular weight are not significant and simultaneously water absorption significantly increases, it should also be expected an increase of polymer elongation at break by the water plasticizing effect.

Figure 7 shows the maximum reproducible tensile strength (190 ± 6.9 MPa) and Young Modulus (3.6 ± 0.1 GPa) obtained in the present work. The comparison of the tensile properties of the sulfonated polyoxadiazoles (SPOD-DPE synthesized for 4-5h) according to the ASTM D 882- 00 with other high performance polymers (PEEK, poly(ether ether ketone); PES, poly(ether sulfone); Vespel®, Poly(pyromellitimide-1,4-diphenyl ether); Torlon®, poly(amide imide); Ultem®, poly(ether imide); LaRC, aromatic poly(imide) [16,17]) according to the ASTM D 882- 00 (marked with * in Fig. 7) as well as according to the ASTM D 638 clearly shows the potential use of this polymer in engineering applications requiring high thermal stability. Durability, long-term performance, hydrolysis and wear resistance, chemical stability are examples of unique characteristics that these polymers should have for suitable engineering applications. In this context, a comparison of the SPOD-DPE with the other polymers presented in Figure 7 is difficult once for each application a specific property will be required. Nevertheless, this work shows that the amorphous SPOD-DPE offers high strength and excellent heat resistance, making it ideal for high strength/ high heat applications.

4. Conclusions

Polyoxadiazoles with sulfonation level (3) in the range 30-60 synthesized through a polycondensation reaction of the hydrazine sulphate salt and a dicarboxylic acid in poly(phosphoric acid) exhibit rigid-ductile behavior with high Young's modulus (3-4 GPa) and with larger elongations at break (up to 120%). Polymer samples with low polydispersity result in higher reproducibility of tensile properties. The tensile strength was shown to be directly affected by the molecular weight and sulfonation values. Sulfonated polyoxadiazoles

with maximum reproducible tensile strength (190 ± 6.9 MPa) can be synthesized in the frame of time of 4-5 h.

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Tables

Table 1. Structural, thermal and mechanical properties of sulfonated polyoxadiazoles.

Figure Captions

Figure 1. Scheme of the polyoxadiazole synthesis

Figure 2. Polymer samples before and after of the shredder.

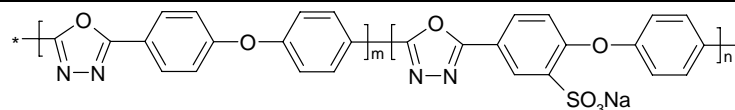
Figure 3. Average molecular weight (M_w) as a function of the reaction time.

Figure 4. Possible reactions that may occur during the POD-DPE synthesis [9].

Figure 5. Tensile strength as a function of molecular weight (insert: T_g as a function of sulfonation level).

Figure 6. Representative stress-strain curve for different reaction times (a) (insert: stress-strain curves for reaction time of 3h); Young's modulus, E , tensile strength, σ_M and elongation at break, ϵ , as a function of reaction time (b).

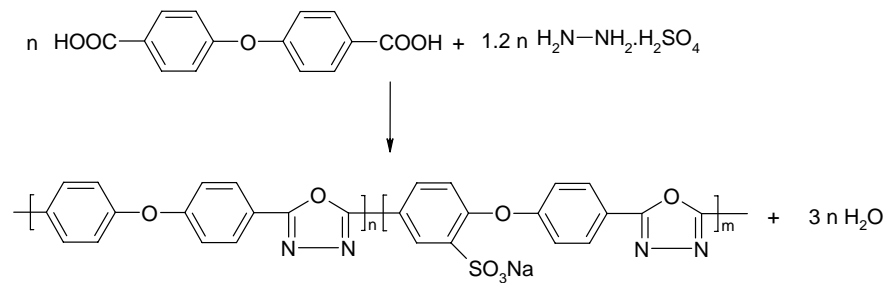
Figure 7. Tensile properties of high performance polymers [16,17].



Reaction time (h)	T_{d5}^a (°C)	Residue ^b (%)	T_g^c (°C)	S/C ^d	SL (%) ^e	M_w (g/mol) ^f	D ^g	Storage modulus (GPa)	
								at 100°C	at 300°C
2	463	79	434	0.074 ± 0.003	38	370 000	2.0	3.08 ± 0.46	2.24 ± 0.27
3	464	79	420	0.065 ± 0.007	34±4	325 000	3.7	3.18 ± 0.48	2.21 ± 0.23
4	466	79	447	0.088 ± 0.003	46	425 000	2.1	3.18 ± 0.10	2.48 ± 0.08
5	469	81	449	0.096 ± 0.001	50	435 000	2.0	4.43 ± 0.19	3.14 ± 0.05
6	468	81	450	0.103 ± 0.001	54	440 000	2.0	3.44 ± 0.07	2.92 ± 0.07
7	470	80	456	0.115 ± 0.001	60	450 000	5.6	3.31 ± 0.21	2.84 ± 0.10

^a 5 % weight loss temperature measured by TGA, ^b Residue weight at 500 °C in N₂, ^c Glass Transition temperature measured by DMTA (tan δ), ^d determined by elemental analysis, ^e Sulfonation level assuming 100% sulfonated when m=0 (S/C=0.19), ^f Average mass molecular weight determined by SEC, ^g Polydispersity.

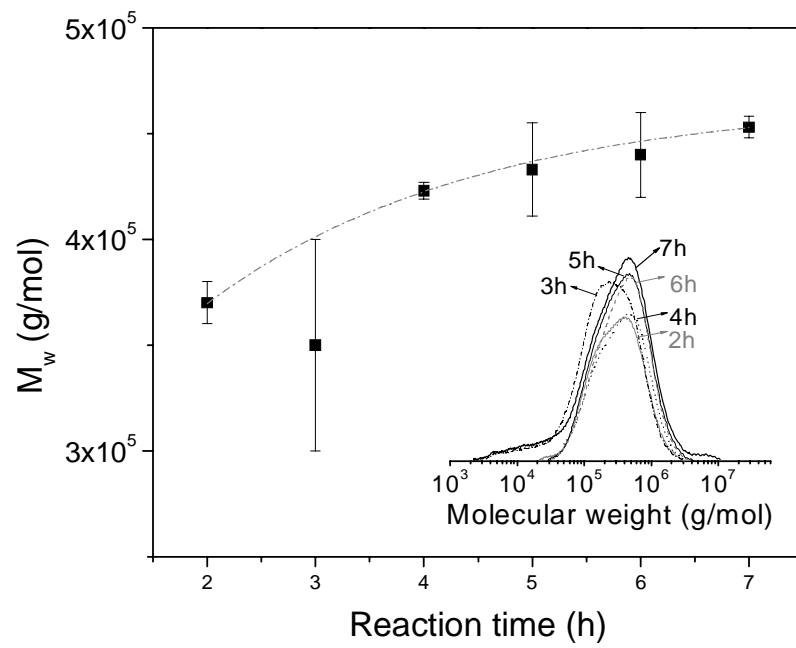
(Table 1)



(Figure 1)

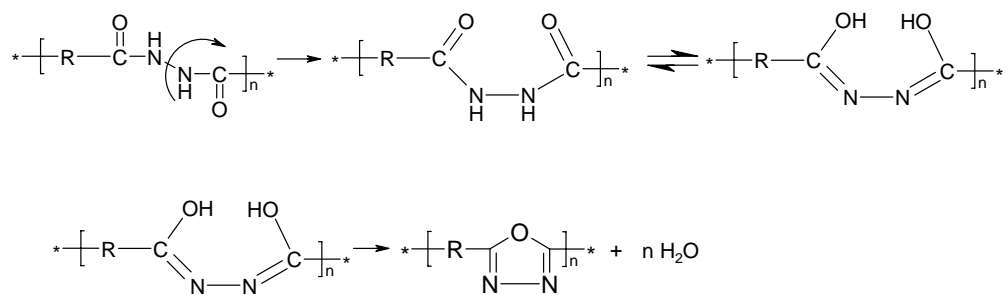


(Figure 2)



(Figure 3)

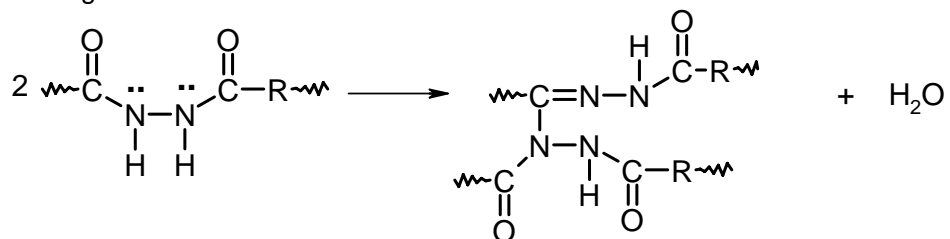
A- Linear cyclodehydration reaction of polyhydrazide into POD



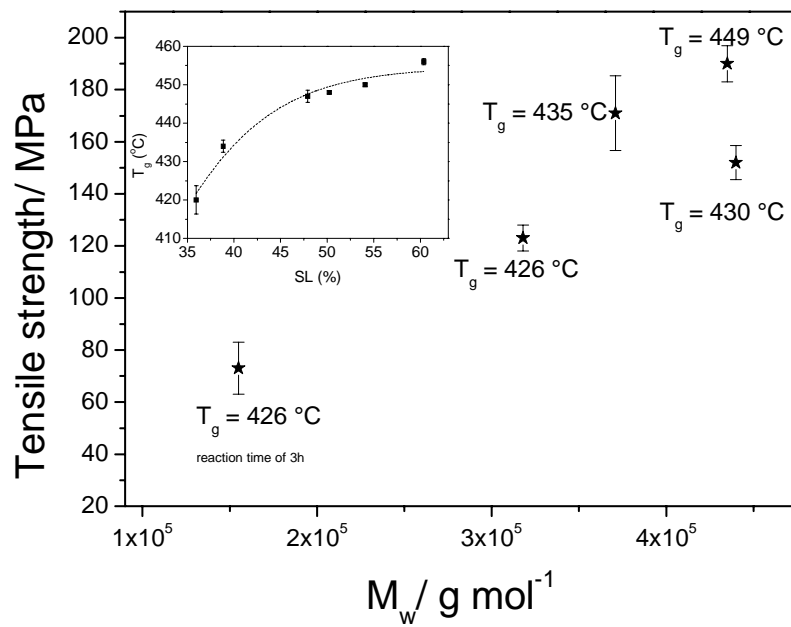
B- Non linear cyclodehydration reaction



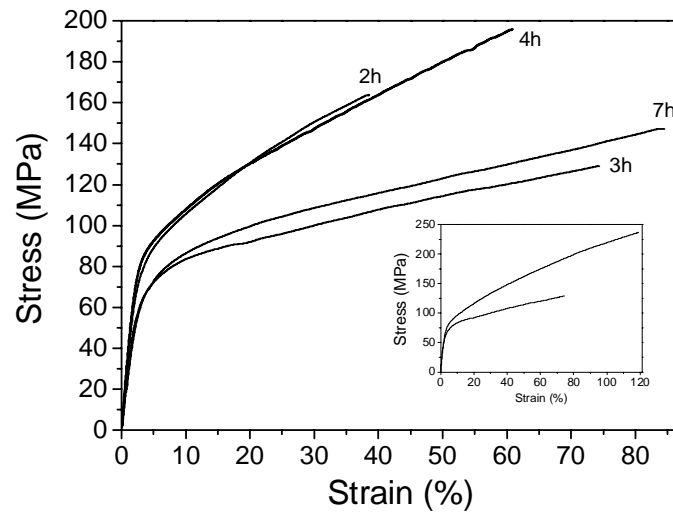
C- Crosslinking reaction



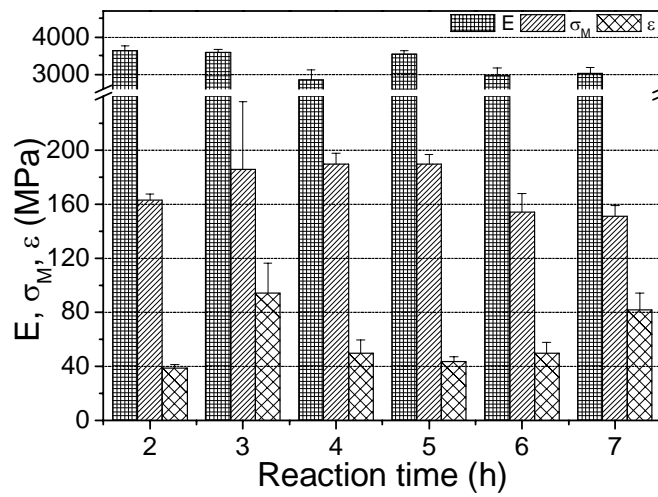
(Figure 4)



(Figure 5)

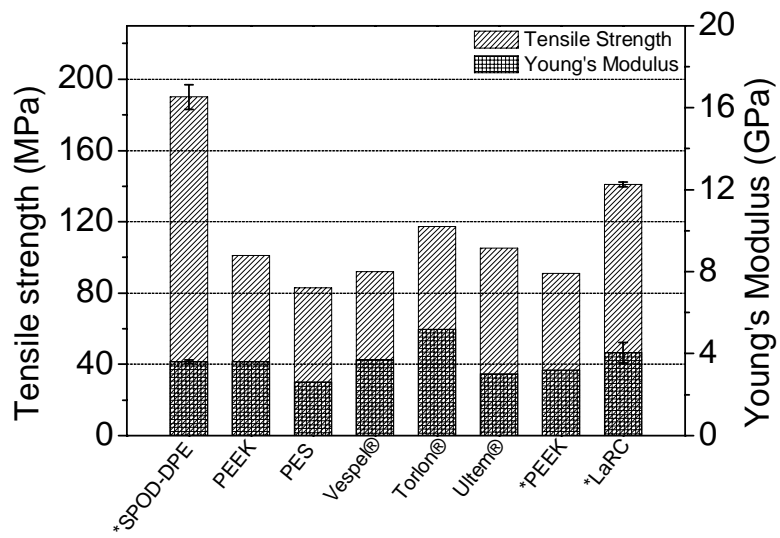


(a)



(b)

(Figure 6)



(Figure 7)