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Synthesis and Thermal Properties of Poly(ethylene glycol)-polydimethylsiloxane Crosslinked Copolymers

(Sintesis dan Sifat Terma Kopolimer Taut Silang Poli(etilena glikol)-polidimetilsiloksana)

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ABSTRACT

Poly(ethylene glycol)-polydimethylsiloxane (PEG-PDMS) crosslinked copolymers with mol ratios PEG:PDMS:Glycerol of 5:3:2, 6:2:2 and 7:1:2 have been prepared and characterized. The synthesis of the copolymers was carried out by the reaction between hydroxyl groups of PEG, PDMS and glycerol with isocyanate groups of 1,6-hexamethylene diisocyanate (HMDI). In the reaction, glycerol was acted as the cross linker. The copolymers were then characterized by FTIR spectroscopy. The thermal behaviour was investigated by DSC and TGA. Based on FTIR results, the crosslinked structure of the copolymers was confirmed by the presence of absorption peak at 3350 and 1710 cm^{-1} which indicated the (-N-H) stretching and carbonyl (-C=O) correspond to urethane links. This showed that the hydroxyl groups of PEG, PDMS and glycerol have reacted to isocyanate groups of HMDI. The copolymers showed melting temperature (T_m) of PEG segments from 22°C to 27°C and glass transition temperature (T_g) from -11°C to -6°C. Meanwhile, the PDMS segment showed values from -53°C to -56°C for T_m , and T_g from -118°C to -122°C. Data obtained from the thermal analysis indicate that thermal stability increases with increasing PDMS mol ratio.

Keywords: Crosslinked copolymer; polydimethylsiloxane; poly(ethylene glycol); thermal

ABSTRAK

Kopolimer taut silang poli(etilena glikol)-polidimetilsiloksana (PEG-PDMS) dengan nisbah PEG:PDMS:Gliserol 5:3:2, 6:2:2 dan 7:1:2 telah disediakan dan dicirikan. Sintesis kopolimer dilakukan dengan tindak balas kumpulan hidroksi PEG, PDMS dan gliserol dengan kumpulan isosianat 1,6-heksametilena diisosianat (HMDI). Dalam tindak balas ini, gliserol berperanan sebagai agen taut silang. Kesemua kopolimer kemudiannya dicirikan oleh spektroskopi inframerah (FTIR). Ciri terma kopolimer dilihat berdasarkan analisis kalorimetri imbasan kebezaan (DSC) dan analisis termogravimetrik (TGA). Berdasarkan spektrum inframerah, struktur taut silang kopolimer ditentukan oleh kehadiran puncak serapan pada 3350 dan 1710 cm^{-1} yang menunjukkan regangan (-N-H) dan kumpulan karbonil (-C=O) yang sepadan dengan pautan uretana. Ini menunjukkan bahawa kumpulan hidroksi PEG, PDMS dan gliserol telah bertindak balas dengan kumpulan isosianat HMDI. Kopolimer menunjukkan suhu lebur (T_m) bagi segmen PEG daripada 22°C hingga 27°C dan suhu peralihan kaca (T_g) daripada -11°C hingga -6°C. Sementara itu, segmen PDMS menunjukkan nilai daripada -53°C hingga -56°C untuk T_m , dan T_g daripada -118°C hingga -122°C. Kestabilan degradasi kopolimer pula meningkat apabila nisbah mol PDMS meningkat.

Kata kunci: Kopolimer taut silang; polidimetilsiloksana; poli(etilena glikol); terma

INTRODUCTION

Polyurethane (PU) is a polymer which consists of urethane links in the main chains. PU can be synthesized by the reaction of polyol, isocyanate and occasionally chain extender is added to modify the properties of the polymer. Segmented PU has been widely studied over the past years because it gives merging of biocompatibility, elastomeric properties and thermoplastic processing conditions (Hong et al. 2010; Wang et al. 2009; Wu et al. 2000). Therefore, it has various applications in industries and daily uses. It has been commercially used as coatings, foams, adhesives, sealants, synthetic leathers, membranes, elastomers, as well as in biomedical applications (Chattopadhyay et al. 2009).

Alternating soft and hard segments in PU suggest distinctive possibilities of designed polymers by varying the block length and composition (Shokrolahi et al. 2014). Thermal stabilities of PU are very important properties which has attracted much attention in the literature over the past decades (Król et al. 2010; Yeh et al. 2010). Soft segment blocks usually have low glass transition temperature (T_g) and normally are polyether or polyester (Hood et al. 2010; Wang et al. 1983). Thermal stability of PU is usually up to 250°C and the hard segments of urethane linkages initiated decomposition (Tyagi et al. 1984). Most of the polymeric materials usually have degradation problems especially at high temperature and it can be resolved by introducing poly(ethylene glycol)

(PEG) segments into the polymer backbone (Sung-II et al. 2000).

PU copolymers with poly(ethylene glycol) (PEG) in the backbone can enhance degradation since PEG has good biodegradability (Kawai 1987; Kawai et al. 1996). Polysiloxanes are versatile materials that have been used in many applications due to its diversity of properties and processing technologies (Askari et al. 2015). Moreover, PU based on polydimethylsiloxane (PDMS) can also overcome the degradation problem (Yeh et al. 2010). PDMS has been widely studied due to its properties such as high heat resistance, good biocompatibility and environmental friendly (Zhang et al. 2013). PDMS has very low glass transition temperature (T_g) which is approximately at -125°C and low surface energy (Clarson et al. 1993). The thermal stability and degradation of polydimethylsiloxane-based PUs have been extensively studied because of the great importance of the PU which lies in its ease of processing and diversity of applications (Chuang et al. 2004; Hamdani et al. 2009).

In this study, poly(ethylene glycol)-polydimethylsiloxane crosslinked copolymer with three different compositions were synthesized by the reaction of terminal hydroxyl groups of PEG, PDMS and glycerol with isocyanate of HMDI. The glycerol was added in the reaction to act as cross linker. The copolymers were characterized to determine the structure and the thermal behaviour. The structure of the copolymers was identified using FTIR spectroscopy. Then, the thermal stability of the copolymers was determined by DSC and TGA. To the best of our knowledge, no study has been reported on the thermal properties of poly(ethylene glycol)-polydimethylsiloxane crosslinked copolymers.

MATERIALS AND METHODS

MATERIALS

Poly(ethylene glycol) (PEG) (M_w 1,500 g/mol), polydimethylsiloxane-bis-hydroalkyl (PDMS) (M_n 5,600), 1,6-hexamethylene diisocyanate (HMDI, 98%) and tin(II)2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$, 95%) were obtained from Sigma Aldrich. Glycerol (M_w 92 g/mol) from R&M Chemicals was used as cross linker. These reagents were used as

received. Chloroform (CHCl_3 , 99%) was obtained from R&M Chemicals and dried over calcium hydride (CaH_2 , Sigma Aldrich) and refluxed prior to use.

SYNTHESIS OF PEG-PDMS CROSSLINKED COPOLYMERS

Poly(ethylene glycol)-polydimethylsiloxane crosslink copolymers (PEG-PDMS PU) with mol ratios of PEG:PDMS:Glycerol 5:3:2, 6:2:2 and 7:1:2 have been prepared by varying the mol ratio of PEG:PDMS and keeping the ratio of glycerol and HMDI constant. PEG and PDMS having two hydroxyl groups at the end of the chain were reacted with isocyanate group of 1,6-hexamethylene diisocyanate such as the following reaction equation in Figure 1.

The synthesis of copolymers was carried out in a 50 mL reaction flask with glass stopcock equipped with magnetic stir bar. First, PEG and PDMS were dissolved in 30 mL of dry chloroform. After that, HMDI was added in the flask. Subsequently, $\text{Sn}(\text{Oct})_2$ catalyst and glycerol were added in the mixture. The ratio of $\text{Sn}(\text{Oct})_2$ added was 1 mol of PEG to 2 mol of $\text{Sn}(\text{Oct})_2$. The reaction was carried out for 3 h at 40°C in inert atmosphere. After that, the synthesized copolymer was casted in Teflon plate with dimensions of 15×15 cm to form a thin film. The plate was left in the fume hood for 24 h to let the solvent dry. Then, the film was peeled from the plate and vacuumed overnight to remove the traces of solvent.

The copolymers were notated as aEbD. E and D were denoted as PEG and PDMS, respectively. Meanwhile, a and b were denoted as the mol ratio of PEG and PDMS respectively. For example, 5E3D indicated that the sample was synthesized by ratio of 5 mol of PEG and 3 mol of PDMS. The three compositions of the copolymers is showed in Table 1.

CHARACTERIZATION

FTIR SPECTROSCOPY

The infrared absorption spectra of the copolymers were obtained by Perkin Elmer Spectrum 400 FTIR Spectrometer. The spectrometer was operated using Attenuated Total Reflectance (ATR) mode. The spectrum were recorded from 4000 to 600 cm^{-1} .

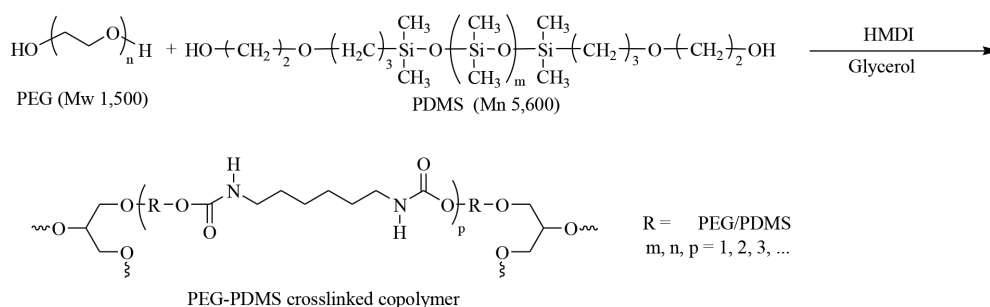


FIGURE 1. Reaction scheme to produce PEG-PDMS crosslinked copolymers

TABLE 1. The composition of PEG-PDMS crosslinked copolymers

Samples	Weight percentage of PEG (%)	Weight percentage of PDMS (%)	Mol ratio PEG:PDMS	Mol ratio HMDI	Mol ratio glycerol
5E3D	30%	70%	5:3	20	2
6E2D	45%	55%	6:2	20	2
7E1D	65%	35%	7:1	20	2

DIFFERENTIAL SCANNING CALORIMETRY (DSC) ANALYSIS

The measurements of glass transition temperature, T_g and melting transition temperature, T_m were carried out by using SII Seiko Instruments Inc. DSC 6200, Japan. The samples were heated at -160°C up to 100°C with heating rate of $15^\circ\text{C}/\text{min}$. The mass of the samples was approximately 5 mg.

THERMOGRAVIMETRY ANALYSIS

The thermogravimetric analysis was performed by using SHIMADZU TA60WS. The samples were heated at heating rate $10^\circ\text{C}/\text{min}$ from 30°C to 600°C under nitrogen atmosphere with flow rate $20\text{ mL}/\text{min}$.

RESULTS AND DISCUSSION

SYNTHESIS OF PEG-PDMS CROSSLINKED COPOLYMERS

The synthesis of PEG-PDMS crosslink copolymers was carried out by reaction of terminal hydroxyl groups of PEG, PDMS and glycerol with isocyanate groups of HMDI. The reaction between these two functional groups will form urethane links. The formation of urethane links showed that the individual homopolymer chain have been linked to the other chain via the links. Since isocyanate can react with hydroxyl group, it also may react with the glycerol to form crosslinked copolymers. There are many possibilities of the selectivity of the reaction. The isocyanate may link the PEG chain with other PEG chain, PDMS chain with other PDMS chain or PEG chain with PDMS. Other possibility was glycerol react with the isocyanate and then reacts with the homopolymer to form a crosslinked structure.

TABLE 2. FTIR absorption bands of PEG-PDMS crosslinked copolymers

Absorption bands(cm^{-1})	Assignments
3350	-N-H stretching
2960-2870	-C-H stretching
1710	-C=O stretching
1540	-C-N-H bending
1620	-C-N stretching
1250	Methyl in $-\text{Si}-\text{CH}_3$

STRUCTURAL DETERMINATION OF THE PEG-PDMS CROSSLINKED COPOLYMERS

The FTIR spectrum of the copolymers that have been obtained are shown in Figure 2 and summarized in Table 2. The absorption at 3350 cm^{-1} is corresponds to (-NH) stretching. In addition, it is found that absorption at 1523 cm^{-1} indicates the (-C-N-H) bending and the absorption at 1736 cm^{-1} is identified as the carbonyl group (-C=O) (Wong & Badri 2010). There is also absorption at 1616 cm^{-1} wavenumber which indicates (-C-N) stretching (Rangel-Vazquez et al. 2014). These results are pointed to the urethane group in the copolymer chain thus confirming that the reaction between the hydroxyl and isocyanate groups has occurred. The sharp peaks at $2960\text{-}2870\text{ cm}^{-1}$ are associated to CH stretching for the copolymers. The absorption peak at 1250 cm^{-1} was assigned to the methyl group of the polydimethylsiloxane.

THERMAL BEHAVIOUR OF PEG-PDMS CROSSLINKED COPOLYMERS

Copolymers generally have two different temperatures of melting transition temperature (T_m) and glass transition

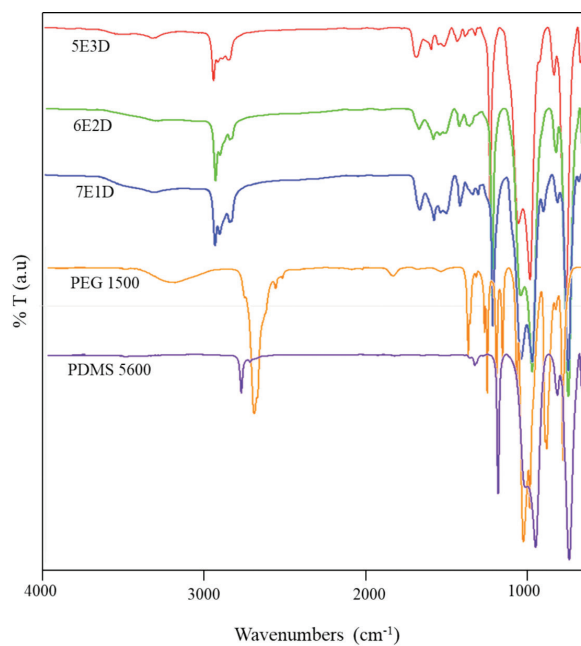


FIGURE 2. FTIR spectrum of PEG-PDMS crosslinked copolymers, PEG 1,500 and PDMS 5,600

temperature (T_g) (Badri et al. 2013). The T_m and T_g of PEG and PDMS segments in the copolymers are summarized in Table 3. In addition, the DSC curves of the copolymers are shown in Figure 3. Comparing between the three copolymers, the T_m value of PEG segments increased from 23°C to 27°C for 5E3D and 6E2D and then decreased

to 22°C for 7E1D. The same trend was also observed for T_g . There is an increment of T_g values for 5E3D and 6E2D from -11°C to -6°C and a reduction to -9°C for 7E1D. However, the T_m and T_g of PDMS segments in the copolymers showed a trend. The values decreased as the mol ratio of PDMS decreased.

TABLE 3. Melting transition temperature (T_m) and glass transition temperature (T_g) of PEG and PDMS segments by DSC

Samples	T_m (°C)		T_g (°C)	
	PDMS segments	PEG segments	PDMS segments	PEG segments
5E3D	-53	23	-118	-11
6E2D	-54	27	-120	-6
7E1D	-56	22	-122	-9

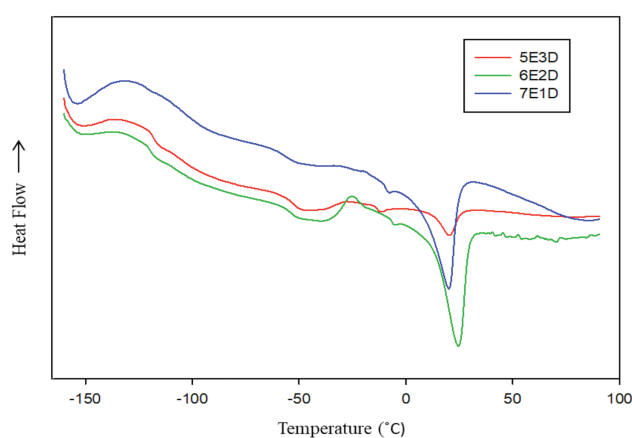


FIGURE 3. DSC curves of PEG-PDMS crosslinked copolymers

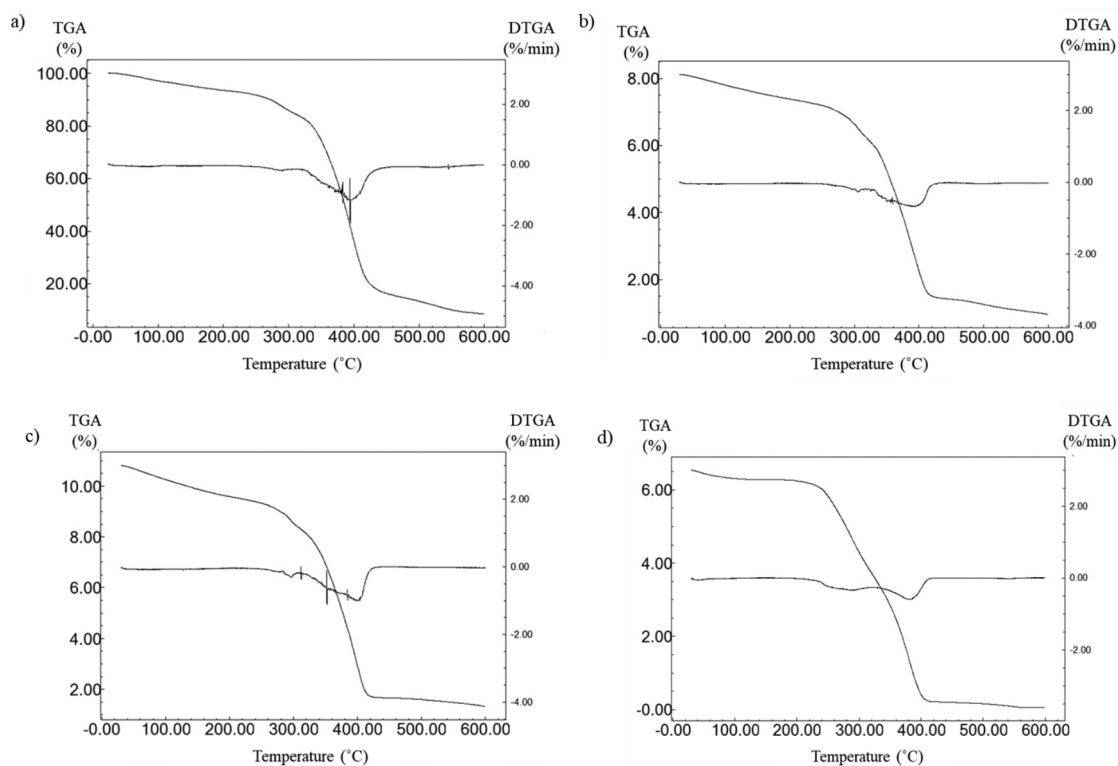


FIGURE 4. TGA/DTGA curves of PEG-PDMS crosslinked copolymers; a) 5E2D b) 6E2D c) 7E1D and d) PEG 1,500

Thermogravimetric analysis was conducted to determine the thermal degradation stability of the copolymers. The TGA and DTGA curves of PEG-PDMS crosslinked copolymers were compared with PEG 1,500 homopolymer, and are shown in Figure 4. Based on the TGA curves in Figure 4, it showed that the small loss of weight at 100°C can be attributed to the loss of moisture. The degradation of the copolymers occurred at higher temperatures compared to PEG 1,500. From the DTG data, the PEG homopolymer used to prepare the copolymer exhibited maximum rate of weight loss at 390°C, whereas the maximum weight loss of the copolymers occurred at higher temperatures of 388°C for copolymer 5E3D, 360°C for 6E2D and 359°C for 7E1D. It can be said that the thermal stability of the copolymers is better compared to the homopolymer. The 5E3D copolymer degrades at higher temperature followed by 6E2D and 7E1D.

CONCLUSION

Three poly(ethylene glycol)-polydimethylsiloxane crosslinked copolymers with different weight ratio of PEG:PDMS were synthesized. The copolymers were synthesized by the reaction of hydroxyl groups of PEG, PDMS and glycerol with isocyanate groups of HMDI. The addition of glycerol in the reaction caused the formation of crosslinked copolymers. FTIR spectroscopy has confirmed that the reaction of hydroxyl and isocyanate groups have taken place. The values of T_m and T_g for PEG and PDMS segments in the copolymers have been obtained by DSC. A trend was seen for the T_m and T_g of the PDMS segment. The temperatures decreased with the decreasing of mol ratios of PDMS. Meanwhile, the degradation stability of the copolymers increases as the mol ratio of PDMS was increased.

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