High Performance Randomly Segmented Poly(Urethane Siloxane) and Poly(Imide Siloxane) Copolymers

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Abstract

Polyimide materials with several kinds of mechanical properties have a great potential to use in aviation and space technology. One of these kinds of polyimide materials is poly(imide siloxane) copolymers. By this work, we also aimed to get flexible substrates in order to use as substrates in solar energy technology. Randomly segmented Poly(imide siloxane) and poly(urethane siloxane) block copolymers were produced based on benzofenon-3,3',4,4'-tetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA) and bis(3-aminopropyl) polydimethylsiloxane (APPS). The ODA and BTDA are the hard segments, APPS and BTDA are the soft segments in the structure. Many kinds of these copolymers could be produced by adjusting the soft and hard segment lengths. Poly(imide siloxane) block copolymers were insoluble in many organic solvents.

Keywords: Flexible Copolymers, Poly(imide siloxane) Block Copolymers, Randomly Segmented Poly(urethane siloxane) Copolymers.
1. Introduction

Flexible substrates are examined to use in flexible solar cells for the industrial purposes. There are three different flexible substrates. One of them is polyimide substrates. Second one is thin flexible metallic substrates. Another one is flexible poly (imide siloxane) hybrid polymer structures. Flexible materials are still used and investigated in solar cell technology. There are three positive sides of polyimide materials. They can compose any hybrid with semiconductor thin film because of the having high Tg values and Polyimide materials are the most preferred materials due to having high Tg ratios. They have the excellent temperature stability. They have high mechanical resistance at composing hybrid and composing as packing type.

Copolymerization is one of the most successful and general methods enables to produce new materials with intended properties during the connection of two structures with different chemical and physical properties in the same polymer chain. Besides, Poly(amide siloxane) monomer blocks which are produced from the combination of Polysiloxane and Polyimide make easier to be processable (Pei,X. et al., 2013). Poly(imide siloxane) has high flexibility and adhesion property and resistant to decompose under any aggressive oxygen environment. For that reason, Poly(amide siloxane) monomer blocks were preferred in the content of this work for the examination of flexible substrates. Polyimides are condensed polymers that are obtained from organic diamines and organic tetracarboxylic acids (or their derivatives). Examination of poly(imide siloxane) flexible substrates are preferred as poly(amide siloxane) monomer blocks which are obtained from the combination of polysiloxane and polyimide enable to processability of polyimide (Pei,X. et al., 2013).

The aim of this study is to examine the use of flexible substrates and the another aim of this research is to make a contribution for increase in the performance of flexibility of polyimide in solar cells by removing low efficiency that is arisen from substrate. For this purpose, APPS was used as the source of Polydimethylsiloxane (PDMS) and block copolymers and polyimide hard and soft blocks were composed in this study.

2. Literature

The use of flexible substrates offers new possibilities for the application of solar cells, for example for building integration by application on uneven surfaces such as tiles. In addition, flexible cells are very thin and lightweight, which makes them also more flexible in use than rigid cells. Also for space applications, flexible solar cells are very attractive, since simpler deployment mechanisms can be used, which saves weight and therefore reduces launch costs significantly (Yang, C.-H. et al., 2011).

Advantage of flexible solar cells, and maybe the most important one, is the potential to reduce production costs. Roll-to-roll deposition is considered more favourable from a production point of view than processing with rigid (glass) substrates. Furthermore, most of the energy and cost required to produce CIGS solar cells on glass is used for the substrate and cover glasses (Yeager J.D. et al., 2008).

Low-cost, glass-free, and thin substrate together with a thin and flexible encapsulant, would combine the advantages of flexible solar cells and cost-effective production. Finally, environmental benefits arise from the expected lower energy pay-back time and reduced module weight if mounted on cars, caravans or RVs. Smaller batteries (e.g. for cars, consumer products) can be used and battery lifetime will be enhanced if recharged and supported by PV sources (Meyer, J.-U., 2001).

The most commonly used substrate for the manufacturing of CIGS-based solar modules is sodalime glass (SLG), which allowed champion efficiencies of up to 19.2% (Ramanathan et al., 2003). This low-cost and well-known material is fabricated on a large scale and with reproducible quality mainly for the window industry (Blain,J. et al., 2007).
3. Experimental

3.1. Materials and Methods

In the content of this study, it is planned to produce flexible poly(imide siloxane) copolymers by adding soft blocks in to Polyamic acid PDMS (polydimethyl siloxane). The chemical materials with properties given in Table 1 were supplied with high purity from Sigma Aldrich.

Table 1. The properties of the used chemical materials.

<table>
<thead>
<tr>
<th>Used Chemical Materials</th>
<th>Synonyms</th>
<th>Molecular Formula</th>
<th>Structural Formula</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methil-2pyrrolidinone</td>
<td>NMP (1 L)</td>
<td>C₅H₉NO</td>
<td></td>
<td>99.13</td>
</tr>
<tr>
<td>Benzofenon-3,3,4,4-</td>
<td>BTDA (5g)</td>
<td>C₁₇H₆O₇</td>
<td></td>
<td>322.23</td>
</tr>
<tr>
<td>tetracarboxylic dianhydride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4’-Oxydianiline</td>
<td>ODA (100 g)</td>
<td>C₁₂H₁₂N₂O</td>
<td></td>
<td>200.24</td>
</tr>
<tr>
<td>Poly(dimethyl siloxane)</td>
<td>APPS (50 mL)</td>
<td>H₂N(CH₂)₃Si(CH₃)₂O[Si(CH₃)₂O]₉Si(CH₃)₃(CH₂)₃NH₂</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>1-2 Dichlorobenzene</td>
<td>ODCB (1 L)</td>
<td>C₆H₄Cl₂</td>
<td></td>
<td>147</td>
</tr>
</tbody>
</table>

Poly(imid siloxane) blocks have high flexibility and adhesion property, has resistant against decomposition in the environment of aggressive oxygen and their thermal crossover temperature is high. Besides, Poly(imid siloxane) has the property of transparent for visible light optically. The randomly segmented and block copolymers were synthesized in the co-solvent system consisting of NMP and ODCB. Hard and soft blocks were mixed. For this purpose, it was planned that to produce block copolymer chains by mixing ODA and BTDA harder blocks and by mixing APPS and BTDA softer blocks. Testing apparatus was presented for synthesis in Fig. 1.
3.2. **Synthesis of Randomly Segmented Copolymers R1**

3.2.1. **Preparation of Randomly Segmented Poly(urethane siloxane) Copolymer R-1**

A flask was charged with BTDA (3.2628 g), NMP (15 mL) and ODCB (10 mL) under nitrogen atmosphere. After the dianhydride was dissolved completely, APPS (3.5261 g) in ODCB (5 mL) and ODA (1.2415 g) were added sequentially.

3.2.2. **Production of Randomly Segmented Poly(urethane siloxane) Copolymer R-1**

The left neck of three necked flask tube was closed. Nitrogen gas was filled in to the flask tube by an injector which is connected to nitrogen gas tank by a hose. 3.26 gr BTDA, 15 mlt NMP (by a 5 mlt pipet), 10 mlt ODCB (by an injector was pulled out) was added in to the three necked flask tube. The mechanical stirrer IKA WERK RW-20 (its mixing level was adjusted to the level 6) was inserted in to the middle neck of the three necked flask tube. The solution was mixed at room temperature. When BTDA anhydride was dissolved completely, ODCB was added in to a different beaker on a heater. While it was being stirred, 3.52 gr APPS was added in to it. Later, 1.24 gr ODA was added, and all addings were stirred on the heater for a while. After that, the last mixture was added in to the first mixture which was in the three necked flask tube (thus, within 45 minutes, first mixture was mixed completely). Total mixture was turned in to light yellow colour. Meantime, inside the flask tube was charged with nitrogen gas. The mixture was stirred at room temperature for 12 h to yield a viscous poly(amic acid) solution. Then the reaction temperature was raised to 185 °C and kept for 8 h. After the requisite time had elapsed, the viscous solution was cooled to room temperature, diluted with NMP and trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, extracted with ethanol and dried under vacuum at 120 °C for 12 h to give the randomly segmented copolymer R-1.
3.3. **Synthesis of Poly(imide siloxane) Block Copolymers B1**

3.3.1. **Preparation of Poly(imide siloxane) Block Copolymers B1**

In the poly(imide siloxane) block copolymers, ODA and BTDA composed the polyimide hard block, while APPS and BTDA composed the polysiloxane soft block. The synthesis of the block copolymer B-1 is used below as an example to illustrate the general synthetic route for the preparation of the block copolymers. A flask was charged with BTDA (0.83 gr), NMP (2.5 mL) and ODCB (2.5 mL) under nitrogen atmosphere. After the dianhydride was dissolved completely, APPS (1.76 g) in ODCB (2.5 mL) was slowly added into the flask.

3.3.2. **Production of Poly(imide siloxane) Block Copolymers B1**

0.83 gr BTDA, 2.5 mL NMP was stirred each other. For this purpose, NMP and ODCB (2.5 mL) were pulled by the injectors and added in to a three necked flask. The volume of the three necked flask tube was 100 mL. On the other hand, 1.76 gr APPS, 2.5 mL ODCB were mixed by a magnetic stirrer within another beaker and then added in to the flask. All necks of the flask were closed. The magnetic stirrer was put in to the mixture within the flask. The nitrogen gas was given to the inner side of the flask from the left neck. The reaction was started to mix by a magnetic stirrer at the room temperature at 6 hours. For that reason, only magnetic stirrer part was adjusted, the temperature part on the device wasn’t adjusted. Later, the reaction temperature was raised to 185 °C and kept for 1 h. After the mixture was cooled to the room temperature, the solution was put into the other flask which contained mixture of BTDA (0.81 gr) and ODA (0.62 gr) had been dissolved in NMP (5 mL) for 6 hours by stirring. During the transfer of the second mixture into the first mixture, ODCB (2.5 mL) was used against any loss of the mixture. The mixture was stirred at room temperature for 12 hours. Then, it was stirred at 185 °C for 8 hours. After all these processes, a hard rubbery structure was formed. The structure was cooled to room temperature and diluted with NMP. It was washed with excess ethanol with stirring. It was collected and again extracted with ethanol. Later, it was dried in vacuum at 120 °C for 12 hours to get the poly(imide siloxane) block copolymer B-1.

4. **Results and Discussion**

The physical properties of flexible substrates were examined. The changes in physical resistance were examined and evaluated. Thus, we aim that an original work on flexible substrates which aren’t examined in literature before and suits space technology is planned. This study has two steps. Firstly, the randomly segmented Poly(urethane siloxane) Copolymers-RI were prepared with BTDA, APPS and ODA by condensation polymerization at room temperature in nitrogen atmosphere. The reaction details are shown in Fig. 2.
The second step, the randomly segmented Poly(imide siloxane) Block Copolymers-B1 were prepared by condensation polymerization at 185°C temperature in nitrogen atmosphere. The reaction details are shown in Fig. 3.

Fig. 2. Formation of Randomly Segmented Poly(urethane siloxane) Copolymers- R1 at room temperature during 12 hours.

Fig. 3. Formation of Poly(imide siloxane) Block Copolymers-B1 at 185°C during 8 hours.
Randomly segmented block copolymers were synthesized in the co-solvent system consisting of NMP and ODCB. APPS was first added to the solution of dianhydride to effectively cap the APPS and then non-siloxane diamine ODA was added to the free dianhydride and anhydride capped APPS. In the randomly segmented copolymer R-1, the APPS was randomly distributed in the polymer chain. As a result, the length of polysiloxane soft block was determined by molecular weight of polysiloxane diamines. The length of polyimide hard block was a function of composition. Thus, the obtained copolymers were called randomly segmented poly(imide siloxane) copolymers (Dogan, T. et al., 2014).

5. Conclusion

In both copolymers, APPS was added to the solution of dianhydride first to cap the APPS. The non-siloxane diamine ODA was added to the free dianhydride and anhydride capped APPS. The polysiloxane diamine APPS was randomly distributed in the randomly segmented copolymer chain. On the other hand, the block copolymers were prepared by first linking two or more APPSs together through BTDA which were linked by dianhydride in the copolymer chain. Anhydride terminated and expanded polysiloxane soft block while this produced soft block was reacted with ODA and additional dianhydride. Poly(imide siloxane) block copolymers had the same APPS content but on the contrary to randomly segmented poly(urethane siloxane) copolymers, extending lengths of polyimide hard block and polysiloxane soft block were adjusted by the creation of monomers.

References