

Study on the Process and Characterization of Thermoplastic Polyamide Elastomers

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ABSTRACT

The advantages of thermoplastic polyamide elastomers (TPAEs) are good physical and chemical properties, simpler processing, lower density, better control of product quality and recycling of scrap. The disadvantages are often requires long synthesis processing, high water absorbency, high monomer and oligomer content. The objects of this research is to modify the structure and process of TPAEs, so as to reduce the processing time, to decrease the monomer and oligomer content, and to enhance the TPAEs water resistance. The synthesis of C36 dimer acid modified TPAEs were done. In a one-step process, C36 dimer acid was mixed with adipic acid as a second chain extender in a reaction which included caprolactam and PTMEG as hard segment and soft segment respectively. The thermal properties of TPAEs were studied by a DSC and TGA, and water absorption of TPAEs were tested to determined the tendency of samples to absorb moisture. Results showed that modified TPAEs with higher C36 dimer acid content have better thermal properties as well as water resistance. We also introduced Nylon 6 as starting materials of TPAEs polymerization . The synthesis of TPAEs was carried out by two-step process. First, Nylon 6 was depolymerized to oligomer, then reacted with PTMEG and added adipic acid as chain extender to form TPAEs. Results showed low degree of TPAEs polymerization and bed properties. It should need further investigation.

Keywords : thermoplastic polyamide elastomers (TPAEs) ; thermoplastic elastomers (TPEs) ; C36 dimer acid ; poly (teramethylene ether) glycol (PTMEG) ; chain extender ; hard segments ; soft segments ; Nylon 6

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REFERENCES

1. 林振煌, 1999, "高性能尼龍聚醯胺彈性體-PEBAX", 塑膠資訊, 28:30-38.
2. 張錫銘, 1999/5/11, "公元2002年全球合成橡膠需求一千兩百萬公噸", 工商時報, 第16版.
3. 吳丁凱, 1988, "熱可塑性彈性體市場及技術", 工研院化工所.
4. 王爾貝, 1997, "聚醯胺類熱塑彈性體經反應押出的改質", 橡膠工業, 21 (3):6-15.
5. 李鍾熙, 1994, "熱塑性彈性體專題調查報告", 工研院化工所.
6. 洪克明, 1994, "熱塑性彈性體市場概況-國內篇", 化工資訊, 8 (6):52-59.
7. 陳文章、顏誠廷, 1997, "熱塑性彈性體- Poly (ether-block-amide) PEBA", 塑膠資訊14:34-37.
8. 劉世忠, 1996, "熱可塑性彈性體業", 華銀月刊, 46 (8):39-41.
9. 日本工業材料月刊, 1996, "熱可塑性彈性體技術課題的挑戰", 石化工業, 18 (5):10-12.
10. 彭正中, 1987, "染料與染色", 台灣中華書局, 台北.
11. 李瓊雲, 1989, "染色學", 復文圖書出版社, 高雄.
12. 謝立生, 1997, "熱可塑性彈性體技術手冊", 高分子工業雜誌社, 台北市.
13. 陳宏謨, 1993, "耐隆6及耐隆66工程塑膠之應用", 化工資訊, 3:38-52.
14. 蔡照雄、?耀國, 秋榮新, 1998, "聚醯胺系彈性體及彈性纖維之製造方法", 專利93972號.
15. 賴耿陽, 1997, "聚?醯樹酯PU原理與實用", 復漢出版社, 台南市.
16. 經濟部技術處, 中國紡織工業研究中心, "尖端科技纖維產品研討會", 經濟部科技研究發展專案計劃 - 紡紗技術開發五年計劃 (三).
17. 陳瑞祥, 1998, "高分子材料於生物醫學領域之應用及展望", 工研院化工所.
18. 健士貿易有限公司, 工程塑膠elf atochem, p.3-6.
19. C. S. Schollenberger and K. Dinbergs, "Thermoplastic Polyurethane Elastomer Molecular Weight-Property Relations" in Advances in Urethane Science and Technology, Vol.7, Technomic Publ.co.,Lancaster, PA,1979, p.1-34.
20. Unchema International "PRIPOL Dimer Acid: Technology & Application" 1997.
21. DSM FIBER INTERMEDIATES, Technical service Caprolactam & Nylon-6, DSM, p.1-9.
22. MACHEREY-NAGEL,

HPLC, Liquid Chromatography, p.46-52. 23. D.J. Sikkema, 1991, "Preparation, Morphology, and Deformation Behavior of Polyoxypropylene-co-Nylon 6 Thermoplastic Elastomers", J. of Applied Polym. Sci.: 43: 877-881. 24. L.Z. Chung, D.L. Kou, A.T. Hu, and H.B. Tsai, 1995, "Blending compositions of polyamides and block copolyetheramides. ", USP 5,416,171. 25. L.Z. Chung, D.L. Kou, A.T. Hu, and H.B. Tsai, 1994, "Preparation of block copolyether-ester-amide.", USP 5,280,087. 26. M. Morton, 1987, " Rubber Technology ", 3rd Ed., p. 453-455, Van Nostand Reinhold, New York. 27. Sifniades et al., 1997, "Process for depolymerizing nylon-containing waste to form caprolactam by superheated steam in the absence of catalyts.", WO 97/20813. 28. Moran, Jr., 1994, "Conversion of nylon 6 and/or nylon 6,6 to monomers", USP 5,310,905. 29. Moran, Jr., et. al., 1995, "Conversion of nylon 6 and/or nylon 6,6 to daipic acid." USP 5,468,900. 30. G.R. Hatfield, Y. Guo, W.E. Killinger, R.A. Andrejad, and P.M. Roubocek, 1993, "Characterization of Structure and Morphology in Two Poly(ether-block-amide) Copolymers", Macromolecules, 26,6350-6353. 31. L.Z. Chung, D.L. Kou, A.T. Hu, H.B. Tsai. 1992. "Block Copolyetheramides. II.Synthesis and Morphology of Nylon-6 Based Block Copolyetheramides. " J. of Polym. Sci. : Part A: Polym. Chem." , 30: 951-953. 32. R.S. Tsai and Y.D. Lee. 1998. " Block Copolyetheresters with Poly (trimethylene 2,6-naphthalenedicarboxylate) Segments: Effect of Composition on Thermal properties. " Journal of Polymer Research. 5 (2): 77-84. 33. R.B. Koch, "Polyether Block Amide", Advances in Polymer Technology.5 (3): 160-162. 34. D.D. Kale, et. al., 1998." Blend of Nylon 6-PET Waste ", Korea Polymer Journal .6 (1): 105-109. 35. Y.C. Yu. and W.H. Jo, 1994. "Segment Block Copolyetheramides Based on Nylon 6 and Polyoxypropylene. I. Synthesis and Characterization." Journal of Applied polymer Science, 54 (5): 585-591. 36. C.J. Wu, J.F. Kuo and C.Y. Chen, 1993 " Rubber Toughened Polyamide 6: The Influences of Compatibilizer on Morphology and impact Properties" Polymer Engineering and Science., 33 (20): 1329-1335. 37. H.J. Liedloff, 1986 "Preparation of Block Polyetherester Amide form Carboxy Terminated Polyamide and Dihydroxy Polyether with Tin Compound Catalyst." , USP46,89,393. 38. D.J. Sikkema , 1991, " Preparation, morphology, and Deformation Behavior of Polyoxypropylene-co-Nylon 6 Thermoplastic Elastomers." Journal of Applied polymer Science, 43 : 877-881. 39. M.F. Pougalan, et. al., 1988, " Perfumed Polymeric Resin Esswntially Consisting of A Polyether-Esteramide. " , USP 4,734,278. 40. R.M. Holsti-mietinen and J.V. Seppala, 1994, " Functionalized Elastomeric Compatibilizer in PA 6/PP Blends and Binary Interactions Between Compatibilizer and Polymer." , Polymer Engineering and Science., 34 (5): 395-404. 41. V.H. Shah, 1983, "Handbook of Plastics Testing Technology", 243-244. John Wiley & Sons, New York.