Enhanced wear performance of ultra high molecular weight polyethylene crosslinked by organosilane

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Ultra high molecular weight polyethylene (UHMWPE) crosslinked by organosilane was thermal compression molded. The organosilane used was the tri-ethyloxyl vinyl silane. Its gelation, melting behavior, crystallinity, mechanical and wear-resisting properties were systematically investigated. The results showed that the gel ratio of UHMWPE increases with the incorporation of organosilane. At a low content of organosilane, the melting point and crystallinity of the crosslinked UHMWPE increase, and hence the mechanical and wear-resisting properties are improved. However, at a high content of organosilane, these performances of the crosslinked UHMWPE become worse. At 0.4 phr silane, the wear resistance of crosslinked UHMWPE reaches its optimum value.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a linear polyethylene with an average molecular weight greater than $2 * 10^6\ \mathrm{g\,mol}^{-1}$. UHMWPE has a wide spectrum of applications, particularly as a material for orthopedic prostheses due to its excellent engineering properties, such as high resistance to chemicals and physical abrasion, low friction coefficient, and high impact strength [1, 2]. Recently, the short-term function of UHMWPE implants has been studied, but their long-term performance has still been a concern for many years [3]. Due to the visco-elasticity of UHMWPE, many problems associated with this polymeric material originate from its inherent weaknesses, like weak creep and fatigue strength compared with metal stem and cortical bone. Therefore, the wear-resistance and anti-creep properties of UHMWPE must be improved in order to provide long-lasting service for active patients. As a result, many attempts have been made by material scientists to improve the wear-resisting and mechanical properties of UHMWPE. One of them, is based on composite technology, i.e. filling with in-organic filler, cement, fiber, etc. [4–10]. For this technology, the dispersion of the filling phase and the interfacial adhesion between various composite components play important roles in determining the wear-resistance of these composites and must be improved. The other approach, that is widely used, involves the peroxide-induced crosslinking (i.e. chemical crosslinking), plasma and γ-ray radiation crosslinking [11–20]. A comprehensive review on chemical-induced and radiation-induced crosslinking was given by Lewis [21]. How to control the degradation of UHMWPE and how to optimize the best crosslinking process are the key factors in implementing the second method successfully.

Organosilane-reduced crosslinking for the modification of polyethylene was developed in the late 1960s and early 1970s, and has been widely used in manufacturing thermal shrinkage films and insulation materials of high voltage electrical cables [22]. One of the advantages is that the molding conditions in this process are less critical than in peroxide and radiation-reduced cross-linking processes. In 1985, Atkinson studied the silane crosslinked polyethylene for orthopedic prosthetic applications [23]. However, little information is available on the organosilane-reduced crosslinking UHMWPE. In the present study, UHMWPE was crosslinked by vinyl tri-ethyloxyl silane with the aim of improving its mechanical and wear resistance properties.

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2. Experimental

2.1. Materials

UHMWPE powder used in this work was supplied by the Second Factory of Auxiliary Agents in Beijing (P.R. China). Its molecular weight is $2.7 * 10^6\ \mathrm{g\,mol^{-1}}$. Vinyl tri-ethyloxyl silane (A–151, produced by the Chemical Factory of Wuhan University, P.R. China) was distilled at atmospheric pressure (b.p. 160–161 °C). The peroxide initiator used was dicumyl peroxide (DCP), which was purified by recrystallization prior to use.

2.2. Sample preparation

UHMWPE powder was mixed with a previously prepared acetone solution of silane and DCP in a high-speed mixer. The amount of silane was varied from 0 to 0.65 phr (part of reagent per hundred parts of UHMWPE), whereas the amount of DCP was kept at the initiator concentration for silane-grafting onto UHMWPE. Acetone in the uniform slurry was removed by evaporating the slurry in an oven at 75 °C for 30 min. This process has been determined to be effective in providing uniform silane and DCP dispersion on the surface of UHMWPE powders, with negligible residual acetone. The above mixtures were compression-molded into plates with dimensions of $180 \times 180 \times 5.0\ \mathrm{mm^3}$ under a pressure of 15 MPa at 200 °C. In this process, vinyl tri-ethyloxyl silane was grafted onto the UHMWPE chain. Then, the silane-grafting UHMWPE plates were immersed in boiling water for at least 8 h. This allows the ethyloxyl groups in the silane to be hydrolyzed to hydroxyl groups. The hydroxyl groups on neighboring chains then condense together to form the silane-induced crosslinking UHMWPE plates.

2.3. Gelation measurement

The percentage of crosslinking can be characterized by the gel ratio. The gel ratio of the silane-induced crosslinking UHMWPE was determined by measuring the insoluble content using the extraction method. Samples were extracted with boiling xylene for 72 h, then washed with ethanol and dried under vacuum at 80 °C to a constant weight. The gel ratio was calculated by the following equation:

$$\text{Gel ratio}(\%) = \frac{\text{Extracted sample weight (g)}}{\text{Sample weight (g)}} \times 100\% \tag{1}$$

2.4. Differential scanning calorimetry (DSC)

DSC measurements were conducted in a Perkin-Elmer DSC-7 instrument at a heating rate of $10\ ^\circ\mathrm{C\,min^{-1}}$ under dry nitrogen atmosphere. Prior to the DSC recording, all samples were heated to 220 °C, and kept at this temperature for 3 min to eliminate the influence of their previous thermal history. After they were quenched to an ambient temperature, the samples were heated from room temperature to 220 °C, and DSC results were recorded.

The degree of crystallinity (X_c) of crosslinked UHMWPE was calculated using the formula below:

$$X_c(\%) = \frac{\Delta H}{\Delta H_{100}} \times 100\% \tag{2}$$

where ΔH is the heat of fusion of the sample, and ΔH_{100} is the heat of fusion for a 100% crystalline sample taken as $289.3\ \mathrm{J\,g^{-1}}$ according to the literature [24].

2.5. Mechanical properties

The silane-induced crosslinking UHMWPE plates were cut into dog-bone shaped tensile bars. The tensile behavior was determined using an Instron tester (model 4206) at room temperature under a cross-head speed of 1 mm/min. Izod impact specimens with dimensions $65 \times 13 \times 5.0\ \mathrm{mm^3}$ were cut from the plates, and were tested by a Ceast pendulum impact tester. Blunt notch with a notch tip radius of 0.25 mm was introduced to the impact specimens with a Ceast notch opener.

2.6. Wear testing

The wear resistance of the silane-induced crosslinking UHMWPE sample is high. Therefore, the weight loss resulting from conducting a pin-on-disc test may be too small to assure the measurement accuracy. In the light of assuring the experimental accuracy and speeding up the test, a wear testing apparatus similar to the one used by Hu *et al.* [25] was used to determine the wear resistance of the UHMWPE samples. As shown in Fig. 1, the plates were cut into a disc of diameter of 60 mm. Four discs were fixed into a stainless steel rod driven by a motor at a rotation speed of 1400 rpm. The wearing medium was a mixture of water and quartz seeds with a size of 8–20 mesh. Water was flowing at a level covering the seeds, which played the roles of transferring and diffusing the heat produced by the friction in the test. The abrasion loss of the sample was calculated by

$$\text{Abrasion loss }(\%) = \frac{W - W_0}{W_0} \times 100\% \tag{3}$$

where W is the weight of the sample after wearing, and W_0 is the weight of the sample before wearing.

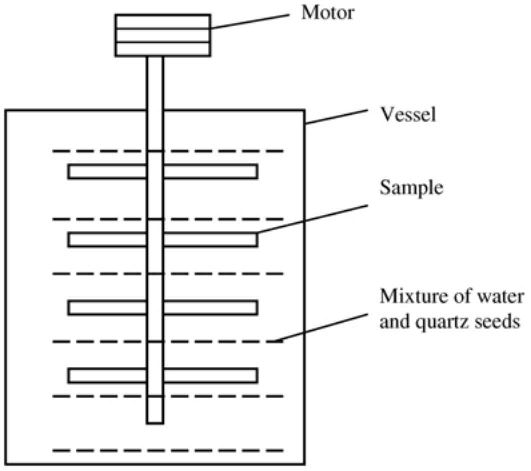

Figure 1 Schematic diagram of wear testing system.

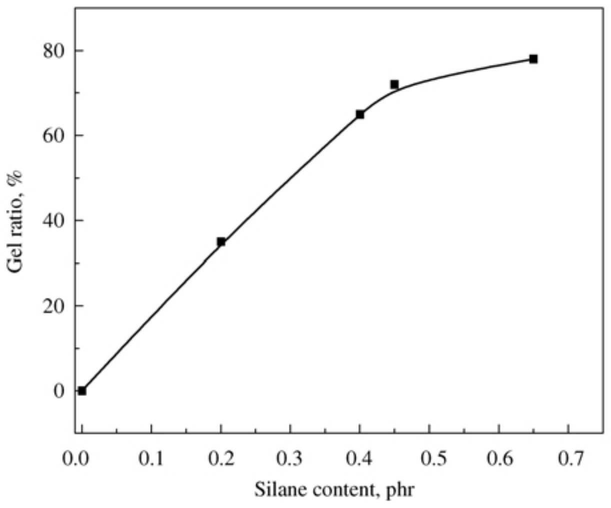

Figure 2 Effect of silane content on the degree of gel of UHMWPE.

3. Results and discussion

3.1. Influence of silane on crosslinking of UHMWPE

As shown in Fig. 2, the degree of crosslinking, as measured by the gel ratio, depends on the silane content. After the UHMWPE is crosslinked by silane, the gel ratio of UHMWPE increases remarkably. Consequently, the crosslinking density of UHMWPE increases. As the silane content is up to 0.45 phr, the gel ratio of UHMWPE is 72%. With further increasing in the silane content, the gel ratio of UHMWPE increases very slowly, and gradually approaches a steady value. It indicates that further increase in the content of silane does not affect the crosslinking density of UHMWPE in the process.

3.2. Thermal properties

The melting temperature (T_m) and degree of crystallinity (X_c) of crosslinked UHMWPEs with different gel ratio were determined from the DSC heating thermograms. The results are shown in Figs. 3 and 4. Apparently, T_m and X_c of crosslinked UHMWPE increase at low density of crosslinking. This result is in accordance with the irradiation behaviors reported by Bhateja [26] and Deng [27]. However, with increase in the density of crosslinking of UHMWPE, T_m and X_c of crosslinked UHMWPE drop significantly. A similar result, determined from irradiation behavior, was reported by Andjejic and Richard [18]. These can be explained by the lamellae and chain structure of UHMWPE.

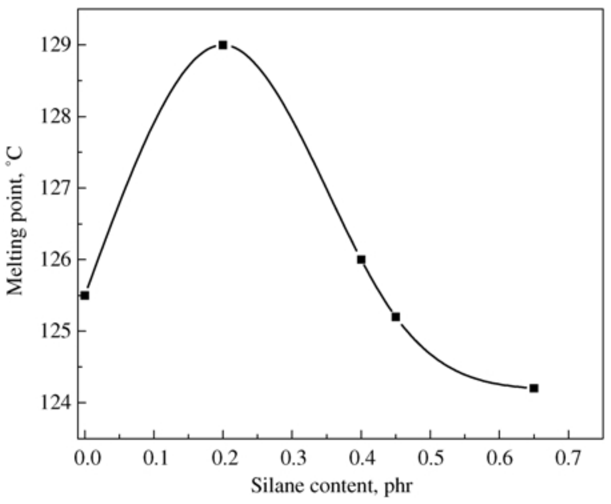

Figure 3 Effect of silane content on melting point of UHMWPE.

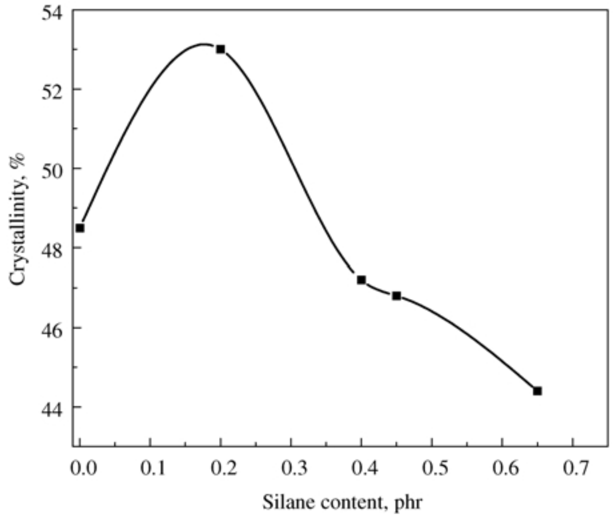

Figure 4 Effect of silane content on degree of crystallinity of UHMWPE.

By measuring the melting point of UHMWPE, the crystalline lamellar thickness, l_c, was estimated using the Thomson–Gibbs equation [28]:

$$T_m = T_{m0}\left(1 - \frac{2\sigma_e}{l_c \Delta H_{100}}\right) \tag{4}$$

where $T_{m0} = 418.7\,\mathrm{K}$ is the melting point for a hypothetical crystal of infinite size for which surface energy effects may be disregarded [24]. The fold surface energy σ_e, that relates to the surface energy of the crystal end faces at which the chains fold [18], was taken as $93 * 10^{-7}\,\mathrm{J\,cm^{-2}}$. The heat of fusion of the crystal ΔH_{100} was taken to be $289.3\,\mathrm{J\,g^{-1}} \approx 289.3\,\mathrm{J\,cm^{-3}}$ [18]. The calculated values of l_c are listed in Table I. In general, larger lamellar thickness corresponds to higher melting temperature, chain regularity and crystallinity, and vice versa. From this table, we can see that l_c increases to 161 Å from 133 Å after UHMWPE is crosslinked by 0.2 phr silane, which leads to the increase in T_m and X_c of crosslinked UHMWPE. With further increase in the content of silane, l_c of the crosslinked UHMWPE decreases, and subsequently, X_c of crosslinked UHMWPE increases at the low density of crosslinking. However, further increase in the density of crosslinking of UHMWPE, the crosslinking networks restrict the motion, fold and crystallization of molecular chains, and hence X_c of crosslinked UHMWPE decreases significantly. Moreover, the higher crosslinking leads to

TABLE I The calculated values of l_c for silane-induced crosslinking UHMWPE

Silane content (phr)	0	0.2	0.4	0.45	0.65
l_c(A)	133	161	137	131	125

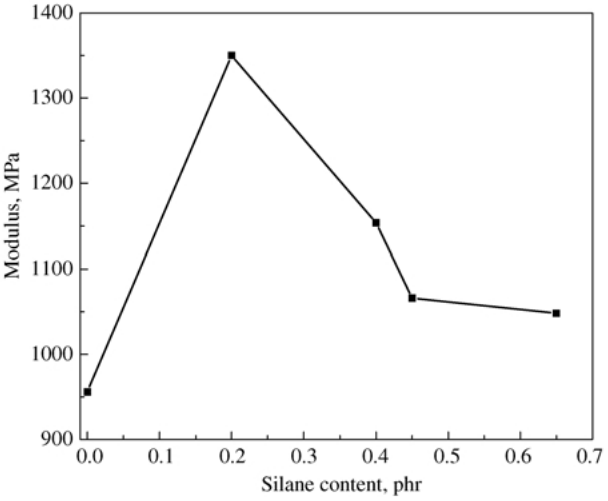

Figure 5 Effect of silane content on tensile modulus of UHMWPE.

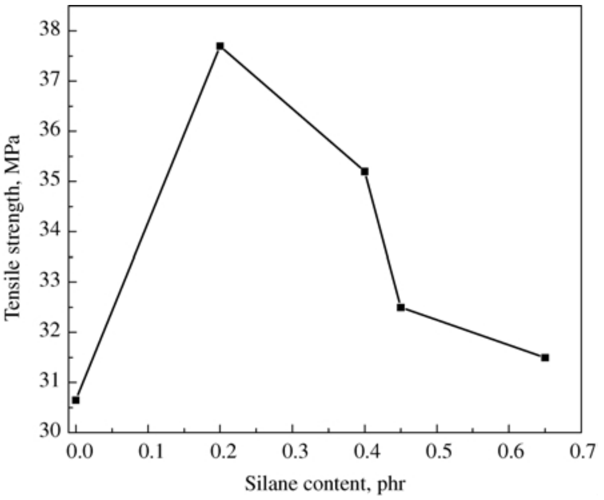

Figure 6 Effect of silane content on tensile strength of UHMWPE.

decrease in the molecular weight between crosslinks [15], and T_m of UHMWPE decreases in turn.

3.3. Mechanical properties

The variation of tensile modulus and strength of the silane-induced crosslinking UHMWPE are plotted against silane content in Figs. 5 and 6, respectively. As shown in Figs. 5 and 6, UHMWPE crosslinked by 0.2 phr silane has higher tensile modulus and strength. It contributes to higher crystallinity, silane-induced crosslinking network formation and hence promotes the number of molecules interconnecting lamellae. As a result, the deformability is limited. With further increase in the silane content, i.e. the crosslinking density, the tensile modulus and strength of the silane-induced crosslinking UHMWPE decrease significantly. These results agree with the irradiation behaviors reported by Kang and Nho [3]. Fig. 7 shows the Izod impact strength of UHMWPE. After UHMWPE is crosslinked by silane, its impact strength decreases owing to the silane-induced crosslinking network formation. The intermolecular networks increase the number of molecules interconnecting lamellae, and restrict the motion of polymer chains, and hence decrease the Izod impact strength of crosslinked UHMWPE.

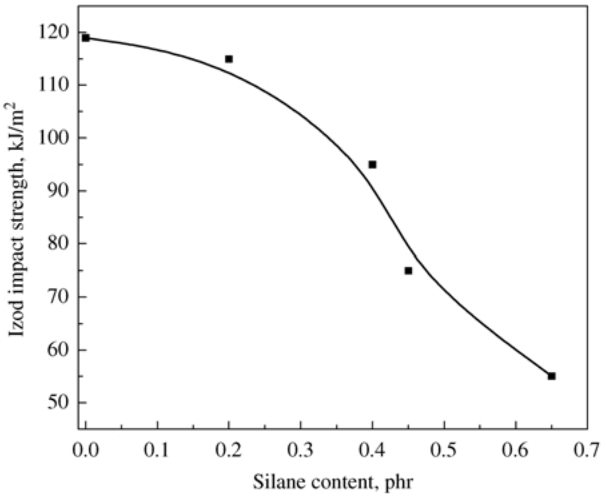

Figure 7 Effect of silane content on Izod impact strength of UHMWPE.

3.4. Wear properties

The variation of abrasion loss of the silane-induced crosslinking UHMWPE is plotted against silane content in Fig. 8. The result shows that the abrasion loss of crosslinked UHMWPE decreases rapidly with the content of silane up to 0.4 phr. However, with further increase in the content of silane, the abrasion loss of crosslinked UHMWPE increases remarkably. In other words, there is a minimum abrasion loss of crosslinked UHMWPE at 0.4 phr silane.

Normally, wear in polymer materials occurs as a result of strong adhesion interaction, abrasive, fatigue, macroshearing, thermal and thermo-oxidative interaction, corrosion, cavitation, etc. [29]. The phenomenon of wear in polymeric material is so complex that a model with fine details is difficult to establish. In practice, a single basic mechanism is always accompanied by the occurrence of other types of wear. The types of wear

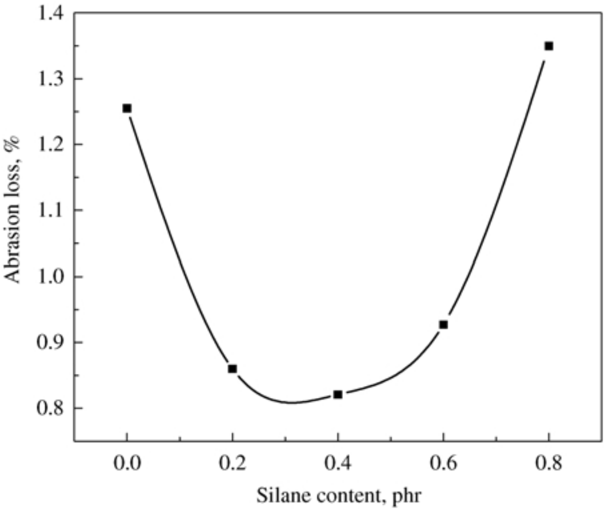

Figure 8 Effect of silane content on wear resistance of UHMWPE.

caused by adhesives and abrasives have been better investigated than the others.

According to the mechanism of adhesive wear [30], the volume of wear can be expressed by

$$\text{Volume of wear} = \frac{kWd}{H} \tag{5}$$

In the case of abrasive wear [30], the volume of wear can be expressed as follows:

$$\text{Volume of wear} = \frac{k_a W d \mu}{H \sigma \varepsilon} \tag{6}$$

where k and k_a are the coefficients of adhesive and abrasive wear, respectively, w is load, d is the sliding distance, and μ is the frictional coefficient. H, α and ε are the hardness, tensile strength and elongation at break of material, respectively.

From Equations (5) and (6), the volume of wear depends upon the bulk properties of polymeric material as well as the surface properties. The higher the mechanical properties of polymer are, the better its wear resistance will be. As mentioned above, the silane-induced crosslinking increases the modulus and tensile strength of UHMWPE at low content of silane, and leads to improvement in its wear resistance. When the content of silane is more than the critical value, the high density of crosslinking decreases the modulus and tensile strength of UHMWPE, which leads to deterioration in wear resistance. Therefore, the silane content at 0.4 phr gives optimum wear resistance for crosslinked UHMWPE.

4. Conclusions

UHMWPEs crosslinked by tri-ethyloxyl vinyl silane were thermal compression molded. Their gelation, melting behavior, crystallinity, mechanical and wear-resisting properties were determined. The results showed that the gel ratio of UHMWPE increases with the incorporation of organosilane. At low content of organosilane, the melting point and crystallinity of the crosslinked UHMWPE increase, and hence all the mechanical and wear resistance properties are improved. However, at high content of organosilane, these performances of the crosslinked UHMWPE become worse. When the amount of organosilane is about 0.4 phr, the comprehensive properties of organosilane crosslinked UHMWPE is optimized.

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References

1. J. CHARNLEY, in ''Low friction arthroplasty of the hip: Theory and Practice'' (Springer-Verlag, Berlin, 1979).
2. E. C. Y. CHING, W. K. Y. POON, R. K. Y. LI and Y. W. MAI, *Polym. Eng. Sci.* **40** (2000) 2558.
3. P. H. KANG and Y. C. NHO, *Radiat Phys. Chem.* **60** (2001) 79.
4. M. DENG and S. W. SHALBY, *Biomat.* **18** (1997) 645.
5. J. SUWANPRATEEB, *J. Appl. Polym. Sci.* **75** (2000) 1503.
6. C. Z. LIU, L. Q. REN, J. TONG, T. J. JOYCE, S. M. GREEN and R. D. ARNELL, *Wear* **249** (2001) 31.
7. H. FUJITA, K. IDO, Y. MATSUDA, H. IIDA, M. OKA, Y. KITAMURA and T. NASKAMURA, *J. Biomed. Mater. Res.* **49** (2000) 273.
8. L. QUE and L. D. T. TOPOLESKI, *Polym. Eng. Sci.* **50** (2000) 322.
9. O. BREUER, A. TZUR, M. NARKIS and A. SIEGMANN, *J. Appl Polym. Sci.* **74** (1999) 1731.
10. N. CHANG, A. BELLARE, R. E. COHEN and M. SPECTOR, *Wear* **241** (2000) 109.
11. O. N. TRETINNIKOV, S. OGATA and Y. IKADA, *Polymer* **39** (1998) 6115.
12. R. M. GUL, *Eur. Polym. J.* **35** (1999) 2001.
13. F. W. SHEN, H. A. MCKELLOP and R. SALOVEY, *J. Biomed. Mater. Res.* **40** (1998) 71.
14. M. GOLDMAN and L. PRUITT, *J. Biomed. Mater. Res.* **40** (1998) 378.
15. O. K. MURATOGLU, C. R. BRAGDON, D. O. O'CONNOR, M. JASTY, W. H. HARRIS, R. GUL and F. MCGARRY, *Biomat.* **20** (1999) 1463.
16. H. MARRS, D. C. BARTON, R. A. JONES, I. M. WARD and J. FISHER, *J. Mater. Sci. Mater. M.* **10** (1999) 333.
17. V. PERMNATH, A. BELLARE, E. W. MERRILL, M. JASTY and W. H. HARRIS, *Polymer* **40** (1999) 2215.
18. S. ANDJEJIC and R. E. RICHARD, *Macromolecules* **34** (2001) 896.
19. H. DONG, T. BELL, C. BLAWERT and B. L. MORDIKE, *J. Mater. Sci. Lett.* **19** (2000) 1147.
20. D. A. BAKER, R. S. HASTINGS and L. PRUITT, *Polymer* **41** (2000) 795.
21. G. LEWIS, *Biomat.* **22** (2001) 371.
22. A. J. PEACOCK, ''Handbook of Polyethylene: Structures, Properties, and Applications'' (Marcel Dekker Inc., New York, 2000).
23. J. R. ATKINSON and R. Z. CICEK, *Biomat.* **24** (1983) 267.
24. B. WUNDERLICH and C. M. CORMIER, *J. Polym. Sci.* **5** Part A-2 (1967) 987.
25. P. HU, Y. X. LU and Q. ZHAN, *Plastics* **19**(4) (1990) 11.
26. S. K. BHATEJA, *Polymer* **23** (1982) 654.
27. M. DENG and W. S. SHALABY, *J. Appl. Polym. Sci.* **58** (1995) 2111.
28. J. D. HOFFMAN, G. T. DAVIS and J. I. LAURITZEN JR. in ''Treatise on Solid State Chemistry'', Vol. 3 edited by N. B. Hannay (Plenum Press, New York, 1976).
29. V. A. BELY, A. I. SVIRIDENOK, M. I. PETROKOVETS and V. G. SAVKIN, in ''Friction and Wear in Polymer-Based Materials'', translated by P. Granville-Jackson (Pergamon Press, Oxford, 1982).
30. R. J. WU, in ''Surface and Interface of Polymer'' (Academic Press, Beijing, 1998).

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