Polym. Korea, Vol. 44, No. 5, pp. 589-595 (2020)
https://doi.org/10.7317/pk.2020.44.4.589
ISSN 0379-153X(Print)
ISSN 2234-8077(Online)

GO 강화 및 조사 가교된 UHMWPE/VE 나노복합재료의 경도와 스크래치 저항의 증가

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(2019년 10월 15일 접수, 2019년 12월 29일 수정, 2020년 6월 1일 채택)

GO Enhanced, Irradiation Cross-linked UHMWPE/VE Nanocomposites with Increased Hardness and Scratch Resistance

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(Received October 15, 2019; Revised December 29, 2019; Accepted June 1, 2020)

Abstract: In this study, a way to reinforce the properties of ultrahigh molecular weight polyethylene (UHMWPE)/vitamin E (VE) nanocomposites was put to use by adding graphene oxide (GO) combined with gamma-ray irradiation cross-linking. The influences of adding GO and irradiation cross-linking treatment on the thermal and mechanical properties were studied, especially the effect of GO doping on irradiation cross-linked UHMWPE/VE nanocomposites. The results show that GO filling has no significant effect on melting temperature and gel content decreased at a small degree, but the crystallinity has been improved obviously. In addition, the ball indentation hardness and scratch resistance were enhanced as well. The comprehensive effects of improved crystallinity and reduced cross-linking degree as well as the good mechanical properties of GO doping were responsible for this result.

Keywords: graphene oxide, UHMWPE/vitamin E nanocomposites, irradiation cross-linking, hardness, scratch resistance.

Introduction

Irradiation cross-linked ultra-high molecular weight polyethylene/vitamin E (UHMWPE/VE) composite has been widely used in total joint arthroplasty (TJA) as its excellent thermal stability, anti-oxidation and wear resistance.[1] However, the existence of VE would stabilize and absorb free radicals generated during irradiation process, which results in the decrease of cross-linking degree of the composite. The decline of cross-linking degree will lead to the decrease of mechanical properties, such as hardness and scratch resistance, and bring about adverse effect to the joint prosthesis in the long-term service. In order to solve those problems, researchers have devoted a lot of efforts, such as Yang and Lee.[2,3] Oral *et al.* studied the irradiation cross-linked UHMWPE blends with 0.1 wt% and 0.3 wt% VE respectively, the result shows that although the oxidation resistance increased, cross-linking degree of the material decreased with the increase of VE content, and mechanical properties reduced as well.[4,5] Besides the cross-linking degree, crystallinity is also one of the factors affecting the properties of materials. Oral *et al.* showed that the tensile and fatigue properties of irradiated cross-linked UHMWPE/VE composites are linearly and positively correlated with the crystallinity.[6] Doshi *et al.* improved the crystallinity of irradiated cross-linked UHMWPE/VE composites to ameliorate the fatigue resistance and tribological properties by high pressure crystallization process.[7] Fu *et al.* researched the influence of high temperature melting treatment on irradiation cross-linked UHMWPE/VE composites, the results show that high temperature melting improved the crystallinity, wear resistance and impact properties also enhanced company with increased crystallinity.[8] Although above methods improved the mechanical and tribological properties to some extent, the high

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cost and tedious process in the preparation process limited large-lot production. Therefore, there are badly in need of a more advanced technique to modify irradiation cross-linked UHMWPE/VE composites.

Graphene with good biocompatibility, mechanical properties and large specific surface area, has been widely applied as a modifier to enforce polymer matrix.[9-12] However, the characteristics of easy clustering and unfavorable dispersal restrict its application. Graphene oxide (GO), a functionalized product of graphene, with excellent dispersion, thermal stability and mechanical properties, has been used as a reinforcing agent for UHMWPE material in recently years. Pang *et al.* fabricated 0.5 wt% UHMWPE/GO composites by hot-pressing, and found that GO is well dispersed in UHMWPE matrix.[13] Moreover, the addition of GO improved not only the thermal performance and crystallinity, but also the hardness of the composites. Ni *et al.* investigated irradiation cross-linked UHMWPE by adding 0.5 wt% GO, showing that the addition of GO slightly increased the melting temperature, but significantly increased the crystallinity.[14] Huang *et al.* studied the irradiation cross-linked GO/UHMWPE composites, and drew a similar conclusion.[15,16] Moreover, the results demonstrated that GO could maintain the efficiency of cross-linking. Furthermore, the mechanical, wear and anti-scratch properties enhanced as well. Besides, other researchers also demonstrate that GO could improve the hardness and wear resistance of UHMWPE.[17-19]

Based on those results mentioned above, we add 0.5 wt% GO into 0.1 wt% UHMWPE/VE composites before irradiation cross-linking. Looking forward to maintaining the cross-linking degree of composites, meanwhile, with excellent thermal stability and higher crystallinity to improve mechanical properties of materials. In order to confirm whether the mechanical properties of irradiation cross-linked UHMWPE/VE/GO composite can be strengthened or not, the ball indentation hardness and scratch test are carried out. Since it is closely related to the mechanical properties of materials, melting temperature, crystallinity and cross-linking degree are also investigated in this study.

Experimental

Materials and Materials Preparation. Powdered UHMWPE (GUR1050) has a density of 0.93 $g\cdot cm^{-3}$ with an average molecular weight of five million and the mean particle diameter of about 140 μm, and was purchased from American Ticina Company. High-purity graphite powder (99.9 wt%, 325 mesh) was provided by Qingdao Jinrilai Co. Ltd. China, and was used to prepare GO. Other chemical reagents were analytical grade and were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd.

GO was prepared in accordance with the modified Hummers method.[20] The irradiation cross-linked UHMWPE/VE/GO composites with the concentration of 0.1 wt% VE and 0.5 wt% GO was fabricated by means of liquid ultrasonic dispersion, high speed ball milling, hot pressing molding and irradiation cross-linked by γ-ray, the detailed steps are as follows: First of all, 0.1 g VE and 0.5 g GO powder were placed in a beaker with 100 mL alcohol solution and ultrasonic treated for 0.5 h, then 99.4 g UHMWPE powder was added into the beaker and continue ultrasonic treated for 1 h to obtain a homogeneous solution. Secondly, the mixed solution was treated by high speed ball milling at a speed of 400 rpm for 2 h and then kept in a water bath at 60 °C to remove the ethanol until the alcohol was completely evaporated. Thirdly, the mixture powder was pressed in a model at 5 MPa for 0.25 h followed by heating treatment at 200 °C for 2 h in a hot air oven, and then pressed at 10 MPa until reached room temperature. Finally, the specimens were cut into different sizes of samples then vacuum packed and irradiated by γ-ray at a rate of 0.5 KGy/h at room temperature, the total irradiation dose was 100 KGy.

Gel Content. According to ASTM D2765-01,[21] the gel content after irradaition cross-linking of UHMWPE/VE/GO composites was calculated in terms of the following formula.

$$\mathrm{Gel} = \frac{W}{W_0} \times 100\% \tag{1}$$

where W_0 is the quantity of sample before test, W is the quantity of sample after test.

Differential Scanning Calorimeter (DSC). DSC (TA, Q200) was applied at a scanning rate of 10 °C/min from 20 to 200 °C in the nitrogen atmosphere. The samples were heated to 200 °C and held for 5 min to remove thermal history; then they were cooled to 20 °C; finally they were heated to 200 °C. The crystallinity of UHMWPE/VE/GO composites was calculated according to the following formula. The crystallinity of UHMWPE/VE/GO composites before/after irradiation cross-linking was calculated according to the following formula.

$$X_\mathrm{c} = \frac{\Delta H}{(1-\phi)\Delta H^0} \tag{2}$$

where ϕ is the filler content, ΔH is the melting enthalpy of

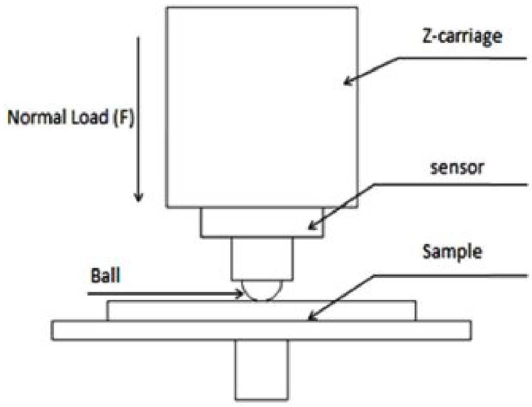

Figure 1. Diagrammatic sketch of ball indentation hardness test.

samples and ΔH^0 is the enthalpy of melting of a 100% crystalline UHMWPE with the data of 293 J/g.[22]

Ball Indentation Hardness. The ball indentation hardness of different composites were measured by the MFT-5000 tribometer and calculated by the following equation according to the standard ISO2 039-73.[23]

$$H = \frac{0.21p}{0.25\pi D(h-0.04)} \tag{3}$$

where H is the indentation hardness of samples (N/mm^2); p is the maximum experimental force (N); D is the diameter of the ball (mm); h is the maximum indentation depth (mm). The diagrammatic sketch of ball indentation hardness test is shown in Figure 1.

Scratch Test. Scratch resistance is also a way to evaluate the mechanical properties of materials. In this paper, the scratch test of different composites was also measured by the MFT-5000 tribometer, the scratch coefficient is calculated by the following equation.

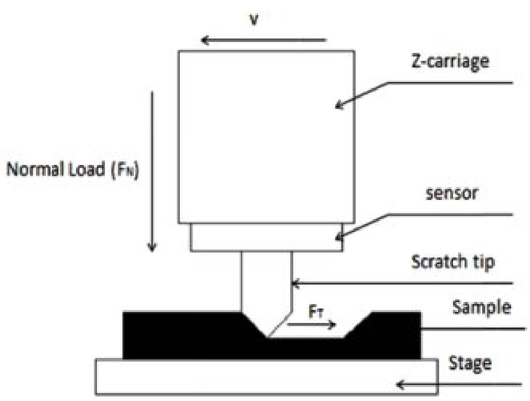

Figure 2. Diagrammatic sketch of scratch test.

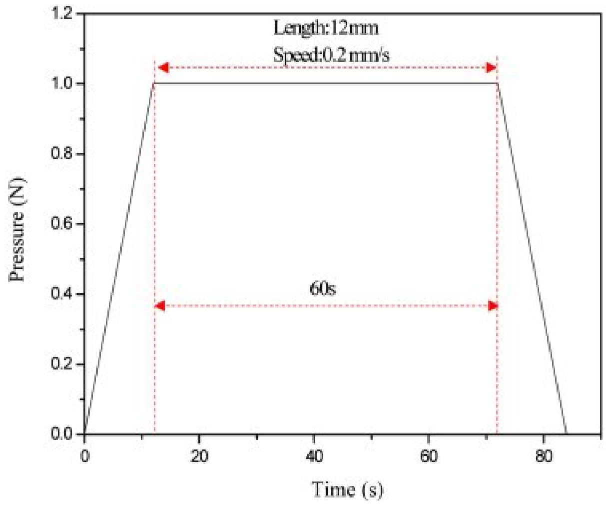

Figure 3. Diagrammatic sketch of parameters for scratch test.

$$\mu = \frac{F_T}{F_N} \tag{4}$$

where μ is scratch coefficient; F_T is the scratch resistance; F_N is normal pressure. The diagrammatic sketch of scratch test is shown in Figure 2.

The experimental load is 1 N with 12 mm scratching length at a speed of 0.2 mm/s, MFD-D profilometer was used to scan the scratch morphology after test. Diagrammatic sketch of parameters for scratch test is shown in Figure 3.

Results and Discussion

As substrate material for artificial joints, UHMWPE composites will release heat which could affect the properties of

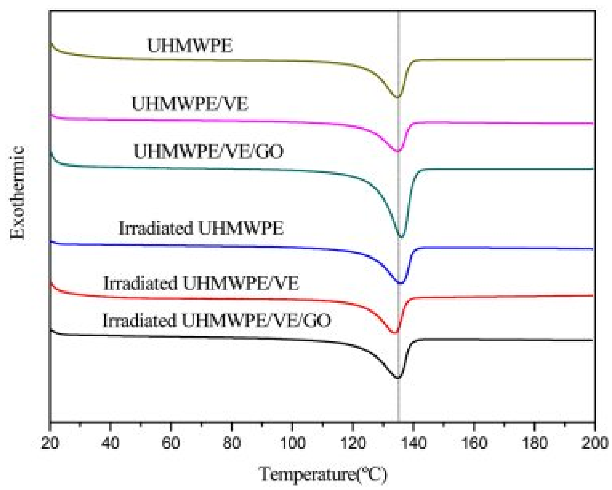

Figure 4. DSC curves of different materials.

Table 1. Melting Temperature and Crystallinity of Different Materials

Materials	Melting temperature (°C)	Crystallinity (%)
UHMWPE	133.7±0.3	50.8±1.5
UHMWPE/VE	133.9±0.2	50.7±1.2
UHMWPEVE/GO	134.2±0.4	53.9±1.1
Irradiated UHMWPE	135.1±0.2	52.5±0.9
Irradiated UHMWPE/VE	134.5±0.4	52.4±1.1
Irradiated UHMWPE/VE/GO	135.2±0.3	54.9±1.3

materials due to friction in long-term applications, in order to characterize the thermal stability of irradiation cross-linked UHMWPE/VE/GO composites, the melting temperature and crystallinity of different composites were studied by DSC, as shown in Figure 4-6 and Table 1. It should be noted that our previous research results show that no degradation of VE occurred at this temperature condition.[24,25] It can be seen that the melting temperature of pure UHMWPE was 133.7±0.3 ºC, the filling of VE and GO has unobvious effect on the melting temperature of UHMWPE. Pang also illustrated the similar results that the filler of both VE and GO has no significant impact on the melting temperature of UHMWPE.[25] After irradiation cross-linking, the trend is almost the same to that of non-irradiated UHMWPE composites. The melting temperature of both UHMWPE and its composites were almost constant, this was due to the cross-linking reaction of the fractured molecular chains in the amorphous region during irradiation, which delays the melting process and increases the melting temperature.[26] GO has capable of grafting to the molecular chain of irradiation cross-linked UHMWPE/VE composites as

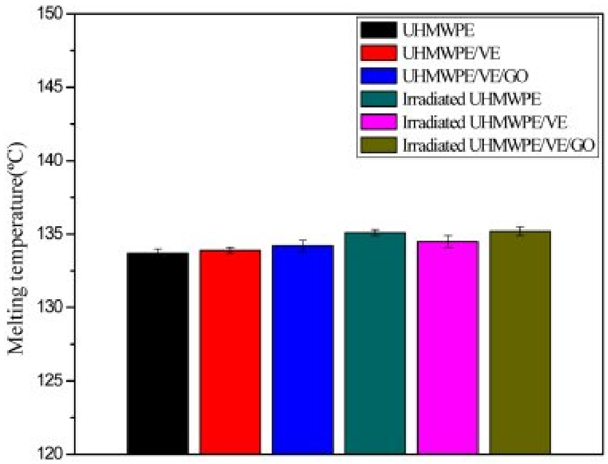

Figure 5. Melting temperature of different materials.

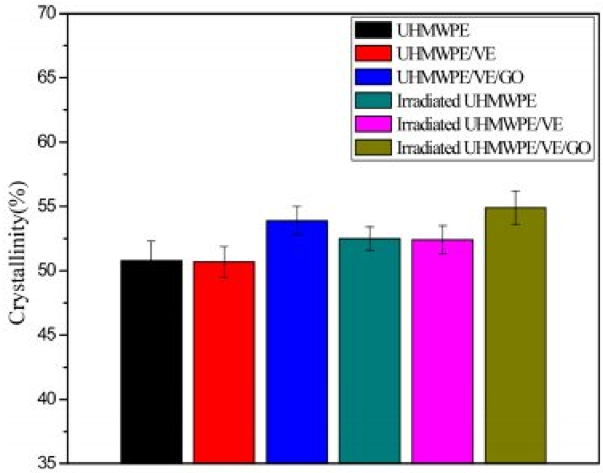

Figure 6. Crystallinity of different materials.

its larger specific surface area, which could be able to enhance interface adhesion of the composites.[27] Therefore, the melting temperature nearly remain unchanged.

As shown in Table 1, the crystallinity of pure UHMWPE was 50.8±1.5 followed with 50.7±1.2 after adding VE, showing that VE filling has no obvious effect on the crystallinity of UHMWPE, this result was analogous to the findings of other researchers.[28] A significantly increased crystallinity emerged in composites after filling GO, compared with that of unfilled. GO can turn into nucleation sites for crystallization as its large specific surface area. In the crystallization process, GO gradually transforms from microcrystalline region to larger crystal region around UHMWPE, which promotes the increase of crystallinity of UHMWPE matrix. In addition, it can be found that irradiation cross-linking not only increased melting temperature but also crystallinity. A large number of fractured molecular chains recrystallized to form more perfect crystals during irradiation, resulting in increased crystallinity. Meanwhile, the crystallinity of irradiation cross-linked UHMWPE was almost the same regardless of whether adding VE or not, showing that VE hardly affects the change of crystallinity. However, the crystallinity improved 4.8% compared with irradiation cross-linked UHMWPE/VE composite after GO filling. On the one hand, irradiation cross-linking disrupts the linear molecular chain of UHMWPE and recrystallizes the broken molecular chain. On the other hand, two-dimensional wrinkled GO with large specific surface area may play a role in hindering the mobility of fractured molecular chains, gathering on the surface of GO and increasing the recrystallization process.[26] It is reported that the increase of crystallinity is beneficial to the improvement of mechanical properties of UHM-

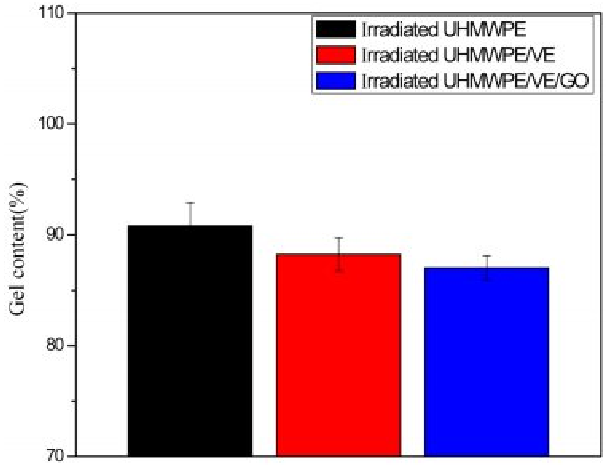

Figure 7. Gel content of different materials.

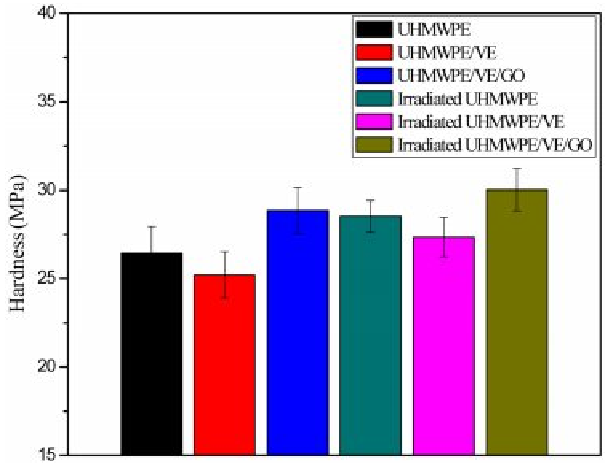

Figure 8. Ball indentation hardness of different materials.

WPE matrix.[6,7,29] Therefore, the experimental results provide an effective theoretical support for further study on the mechanical properties of irradiated cross-linked UHMWPE/VE/GO composites.

To a certain extent, cross-linking of composites can improve mechanical properties. Therefore, for the sake of characterizing the cross-linking degree of irradiated cross-linked UHMWPE/VE/GO composites, the gel content of the composites was tested, as shown in Figure 7. The gel content of irradiation cross-linked UHMWPE was 90.25% and with 2.9% decline after adding VE, the result was similar to Oral.[5] This was due to the ability to absorb and stabilize free radicals of VE, hindering the cross-linking of free radicals. After adding GO, the gel content of the irradiated cross-linked UHMWPE/VE/GO composite decreased slightly, but it was not obvious. This may be that the mobility of fractured molecule chain was hindered by the strong interface binding force between GO and UHMWPE/VE matrix.[14,26] Once more, to some degree, GO composite has the function of scavenging free radicals. In addition, Hyun studied the effect of γ-rays on the crystallinity of UHMWPE under different crystallization conditions.[30] It was found that the crystallinity of UHMWPE increased whereas the amorphous region of UHMWPE decreased, limiting the cross-linking of UHMWPE.[31] To be specific, GO has moderating effect on gel content influencing the composites, but the effect is not very significant.

Figure 8 shows the ball indentation hardness of irradiation cross-linked UHMWPE/VE/GO composites. It can be found that the filler of VE reduced the hardness of UHMWPE slightly, but the hardness of the composites increased significantly after GO filling. The hardness of pure UHMWPE is 26.43 MPa, then decreased to 25.21 MPa after filling VE and increased to 28.86 MPa after filling GO. This was owing to the excellent mechanical properties of GO, its wrinkled two-dimensional structure can withstand part of the loads and transfer them to a larger layered structure.[13-16,26] Although the hardness of the composites decreased after filling VE, the addition of GO played a dominant role, and the combined effect of those two factors resulted in the increase of the hardness. Irradiation cross-linking increases the hardness of pure UHMWPE by 7.9%, and the hardness of irradiation cross-linked composites changed from 27.34 MPa to 30.03 MPa after filling VE and GO, respectively. This is due to the absorption of free radicals by VE, resulting in the decrease of cross-linking degree.[26] Although the cross-linking degree of irradiated cross-linked UHMWPE is reduced by adding VE, which is not conducive to the increase of hardness, UHMWPE inevitably oxidizes and becomes brittle during irradiation process, which also reduces the hardness of the material. The existence of VE effectively improves the oxidation resistance of the material, and the two functions make the hardness decrease in a very small range. As the excellent mechanical properties of GO, the irradiation cross-linked UHMWPE/VE/GO composite possesses optimal hardness compared with other materials. Furthermore, Buchanan pointed out that the hardness of material is closely related to its crystallinity and increases with the increased crystallinity, which is similar to our research.[31] In addition, although GO filling slightly reduces the cross-linking density of irradiation cross-linked UHMWPE/VE composites, whereas improves the hardness, indicating that crystallinity plays a leading role in improving hardness of the materials.

Figure 9 and Figure 10 show the scratch coefficient and

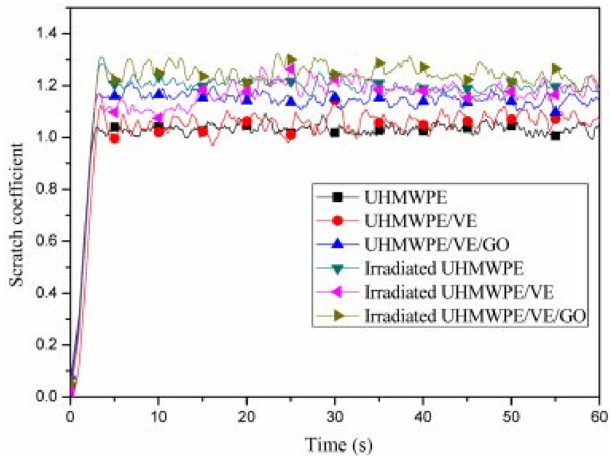

Figure 9. Scratch coefficient of different materials.

Table 2. Scratch Data of Different Materials

Materials	Mean scratch coefficient	Scratch depth (μm)
UHMWPE	1.01±0.02	22.8±1.3
UHMWPE/VE	1.02±0.01	22.7±1.5
UHMWPEVE/GO	1.12±0.01	20.5±1.7
Irradiated UHMWPE	1.17±0.02	18.3±1.1
Irradiated UHMWPE/VE	1.14±0.01	19.2±1.9
Irradiated UHMWPE/VE/GO	1.21±0.02	16.4±1.5

morphology of irradiation cross-linked UHMWPE/VE/GO composites, the specific data are shown in Table 2. The result shows that the mean scratch coefficient vary from 1.01 to 1.21, and hardly changed after adding VE. It can be found that the addition of VE has no effect on the scratch coefficient of pure UHMWPE, which is mainly due to the unchanged crystallinity. However, the addition of GO led to an increase of scratch coefficient of 11%. The wrinkled two-dimensional structure of GO and the increased hardness of composite increase the sliding resistance of probe in the matrix, the tiny van der Waals force between GO slice and UHMWPE matrix is also one of the reasons for the increase of scratch coefficient.[13] After irradiation cross-linking, the mean scratch coefficient increased to 1.17, it can be attributed to the cross-linking degree. The molecular chains interrupted by γ-rays are recombined and cross-linked, which increases the crystallinity and cross-linking degree of the matrix, the increase of hardness resulted in the increase of scratch coefficient.[15,16] Compared with irradiation cross-linked UHMWPE, the scratch coefficient is reduced by 3% after filling VE, this is mainly due to the decrease of cross-linking degree. The irradiation cross-linked UHMWPE/VE/GO composite possesses maximum scratch coefficient. On the one hand, the increased cross-linking degree and the addition of GO increase the sliding force of probe, respectively. On the other hand, while the UHMWPE molecular chains are interrupted during irradiation process, the GO molecular chains are also interrupted generating GO free radicals simultaneously, partial GO free radicals react with UHMWPE radicals to form C-C bonds.[14] The bond energy of the generated C-C bond is much stronger than that of the van der Waals force, resulting in increased interface bonding force, which further increased the scratch coefficient. Consequently, those above factors result in the biggest scratch coefficient of the irradiation cross-linked UHMWPE/VE/GO composite.

Compared with scratch coefficient, scratch depth presents the opposite results, the scratch depth decreased from 22.8 to 16.4 μm, as shown in Table 2. UHMWPE possesses the biggest depth, the addition of VE had no obvious effect on the scratch depth of pure UHMWPE, however, irradiation cross-linking and GO filling reduce the scratch depth obviously. The

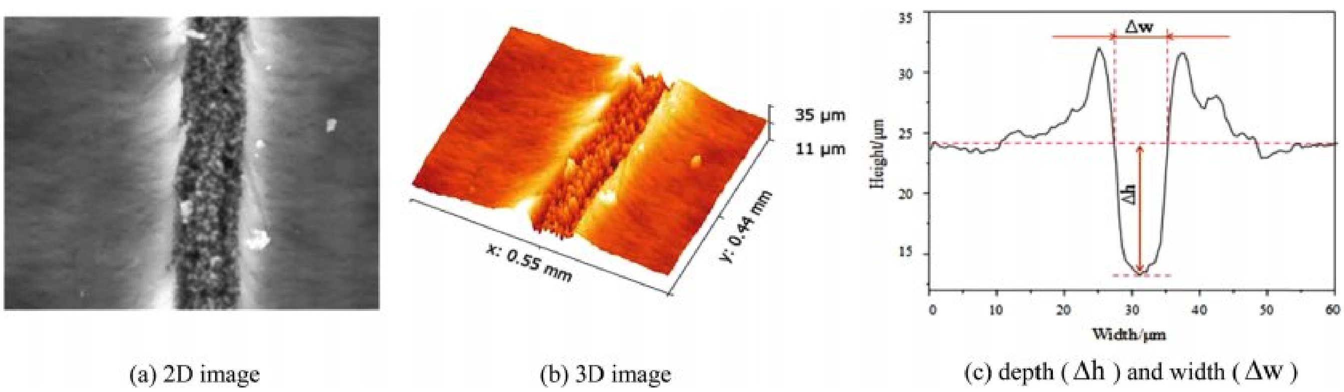

Figure 10. Scratch morphology of different materials.

reason for this phenomenon is similar to that of scratch coefficient.

Besides, another reason for the improvement of mechanical properties may be nanoinclusion and nanoconfinement effects caused by the addition of GO, as reported by Kim and Choe.[32,33] After adding 0.5 wt% GO, composites reveal improved mechanical properties owing to strong polymer–filler interactions by virtue of large contact area caused by GO nanosheets. Since nanoinclusion and nanoconfinement effects of interface boundary, UHMWPE polymer and GO nanosheet composites have a very broad application prospects in strengthening mechanical properties by increasing the interfacial area.

Conclusions

The emphasis of this work is the study of GO improving the mechanical properties of irradiation cross-linked UHMWPE/VE composites. Adding GO into UHMWPE/VE composites before irradiation cross-linking provided a practicable approach to improve mechanical properties of irradiated UHMWPE/VE composites while obtaining high hardness and scratch resistance. In this study, irradiation cross-linked UHMWPE/VE composite was enhanced by filling GO. VE filling decreased the gel content, resulting in a slight decrease of hardness and scratching performance. The addition of GO slightly affected the melting point and gel content of the composite, but to a small extent. However, crystallinity shows distinct improvement. Due to the great mechanical properties of GO, the hardness and scratch resistance improved 19.8% and 28.1%, respectively. Meanwhile, irradiation cross-linking and GO filling can synergistically enhance the thermal stability and mechanical properties of UHMWPE/VE composites.

Acknowledgments: This study is supported by the Additive Manufacturing Products Supervision and Inspection Center of Jiangsu Province, Wuxi Institution of Supervision & Testing on Product Quality, Wuxi, China.

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