Investigation of the oxygen depletion properties of low density polyethylene resins filled with thermally stable oxygen scavengers

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ABSTRACT

The thermal stability, oxygen depletion and tensile properties of low density polyethylene (LDPE) resins filled with ascorbic acid (Vc), sodium ascorbate (SA), iron (Fe) and modified iron (MFe) oxygen scavengers were systematically investigated. Thermogravimetric analysis (TGA) results clearly suggest that the thermal stability of SA powder and $L_{95}(SA)_5$ specimen is significantly better than that of Vc powder and $L_{95}(Vc)_5$ specimen, respectively. The oxygen depletion efficiency of $L_{95}(SA)_5$ is significantly better than that of $L_{95}(Vc)_5$, $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ specimens, although the virgin SA powders exhibit worse oxygen depletion efficiency than Vc, Fe or MFe powders before melt blending. Moreover, at a fixed weight ratio of Vc (or SA) to MFe of the oxygen scavenger compounds, the oxygen depletion efficiency of L95[SAx(MFe)y]5 series specimens is always significantly better than that of L95[Vcx(MFe)y]5 series specimens. In fact, at weight ratios of Vc/MFe and SA/MFe higher than 3/7 and 5/5, respectively, the residual oxygen concentration values present in the airtight flask of L95[Vcx(MFe)y]5 and L95[SAx(MFe)y]5 series samples at any time are even lower than those of the L95(Vc)5 and L95(SA)5 specimens, respectively. Further tensile experiments show that the tensile properties of the L95[SAx(MFe)y]5 series samples are always higher than those of the corresponding L95[Vcx(MFe)y]5 series samples with the same loadings of oxygen scavenger compounds, respectively. In order to understand these interesting thermal stability, oxygen depletion and tensile properties of these LDPE oxygen-scavenging plastics, scanning electron microscope and energy dispersive X-rays analysis of the compositions on the surfaces of L95[SAx(MFe)y]5 and L95[Vcx(MFe)y]5 series samples were performed. Possible reasons accounting for these interesting properties of these LDPE oxygen-scavenging plastics are proposed.

Keywords: oxygen depletion, LDPE, oxygen scavenger

1. INTRODUCTION

"Modified atmosphere packaging (MAP)" technology [1] has being used to reduce the oxygen contents and improve the shelf life of food contained in package for the past two decades, wherein the "passive" and "active" packaging technologies were used in the MAP technology. Barrier plastic materials, such as poly (ethylene terephthalate), polyamide, polyvinylidiene chloride, and ethylene-vinyl alcohol copolymer are often used as key components in the "passive" packaging technology [2-14] to enhance the oxygen permeation resistance of plastic packages. Nevertheless, barrier plastic packaging materials can't prevent permeation of oxygen completely. In contrast to the barrier plastic materials, active packaging materials contained oxygen scavengers can react with oxygen that was trapped in the plastic packaging materials or permeated into the packages [15], and hence, offer safety and savings [16]. By using the active packaging technology, quality changes of oxygen-sensitive foods can often be minimized [17-18].

Inorganic and organic types of oxygen scavengers have being used in the active packaging technology. Iron, sodium hydrosulfite, platinum materials are well known inorganic oxygen scavengers [19-21]. In contrast, yeast, ascorbic acid

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(vitamin C, Vc), enzyme and photo-sensitive dye were often used as organic oxygen scavengers in the literatures [22-27]. In which, iron powder and ascorbic acid are the most often used oxygen scavengers in the food packaging. Iron-based oxygen scavenger reacts with oxygen and loses its ability of oxygen depletion quickly due to its high activity. In contrast to iron powders, the ascorbic acid oxygen scavengers are often added directly into liquid food or beverage as an efficient oxygen scavenger, however, its oxygen depletion rate is slow unless it is catalyzed by the transition metals [28]. As reported by several investigators [26-31], the oxygen removing rates of the ascorbic acid can be accelerated by the presence of transition metal ions, such as, Cu^{2+} and Fe^{2+} etc.. However, very few investigations [26, 27] have ever reported on the chemistry and composition of oxygen-scavenging plastics in peer-reviewed journals. In our recent investigations [26], the sodium chloride was used to modify and accelerate the oxygen depletion rates of the iron powders. In additional to iron powder, ascorbic acid was compounded with the modified iron (MFe) powders to prolong the oxygen removing efficiency of the MFe/Vc oxygen scavenger compounds filled EVA specimens. Our latest study [27] further indicate that the oxygen depletion rates of MFe/Vc oxygen scavenger compounds filled EVA specimens increase significantly as the particle sizes of MFe powders reduce. However, it is worth noting that a "synergistic" effect on the oxygen depletion properties of the MFe/Vc oxygen scavenger compounds filled EVA specimens was observed, as their weight ratios of Vc to MFe are between certain optimum ranges. In fact, the oxygen-scavenging resins with better oxygen depletion properties always result in lower peroxide values for modeled food samples stored in the airtight flasks of E_{VcMFe} series samples.

However, in comparison with MFe or other inorganic oxygen scavengers, Vc is significantly less stable during the compounding processes of many packaging plastics (e.g. LDPE, EVA etc.), that can reduce the oxygen depletion efficiency of the oxygen scavenging plastics.

In this investigation, sodium ascorbate (SA) with relatively high thermal stability was chosen to replace Vc in the novel Vc/MFe oxygen scavenger compounds. The main objective of this study is to compare the thermal stability and oxygen depletion properties of LDPE resins filled with Vc/MFe and SA/MFe oxygen scavenger compounds. Possible mechanisms accounting for these interesting thermal stability, oxygen depletion and tensile properties of LDPE oxygen-scavenging plastics are proposed.

2. EXPERIMENTAL

2.1 Materials and sample preparation
The low density polyethylene (LDPE) resins with a trade name of Q281 were obtained from Sinopec Shanghai Petrochemical Company, China. The ascorbic acid, sodium ascorbate and iron powders used as the oxygen scavengers were purchased from Tianjin Chemical, Zhengzhou Tianjian Chemical and Chengdu Sagewell Science Corporations, respectively. As reported in our previous studies [26, 27], the iron powders were mixed with 20% sodium chloride (NaCl) solution at a weight ratio of 40 to 1 to accelerate their oxygen removing properties. The NaCl treated iron powders will be referred to as the modified iron (MFe) powders in the following discussion. The MFe powders were then dried in a vacuum oven at 80oC for 4 hours to remove the residual water.

The oxygen absorbable resins were then prepared by melt-blending LDPE resins with a total combined weight of 5 wt% of MFe/ascorbic acid or MFe/sodium ascorbate compound powders. Before melt-blending, LDPE was dried in the vacuum oven at 80 oC for 8 hours, and then blended with varying compositions of oxygen scavengers and/or oxygen scavenger compounds using a SU-70 Plasti-Corder Mixer, which was purchased from Suyuan science and Technology Corporation, Chang Zhou, China. The 70 ml Plasti-Corder Mixer is equipped with a co-rotating, intermeshing twin screw with a diameter of 30mm and L/D ratio of 10. During each compounding process, the Plasti-Corder Mixer was operated at 150 oC and a screw speed of 120 rpm for 1 minute. The compositions of oxygen absorbable resins prepared in this study were summarized in Tables 1 and 2. The oxygen absorbable LDPE resins were then hot-pressed at 150 oC and 10Mpa for 1 minute and then cooled at room temperature. The film thickness of the oxygen absorbable LDPE films is about 0.3 mm.

2.2 Thermogravimetric analysis
Thermogravimetric analysis (TGA) was conducted with a PerkinElmer TGA 7 connected with thermal analyst 2000 system under N_2 at a purge rate of 40 ml/min. Samples were heated from room temperature to 700 ^{o}C at a heating rate of 10 ^{o}C /min.

Table 1 The compositions of $L_{95}[Vc_x(MFe)_y]_5$ specimens blended with varying amounts of ascorbic acid and MFe.

Sample	LDPE (phr)	Sodium ascorbate (Vc) (phr)	MFe$_l$ (phr)
$L_{95}(MFe)_5$	100	0	10
$L_{95}[Vc_1(MFe)_9]_5$	100	1	9
$L_{95}[Vc_3(MFe)_7]_5$	100	3	7
$L_{95}[Vc_5(MFe)_5]_5$	100	5	5
$L_{95}[Vc_7(MFe)_3]_5$	100	7	3
$L_{95}[Vc_9(MFe)_1]_5$	100	9	1
$L_{95}(Vc)_5$	100	10	0

Table 2 The compositions of $L_{95}[SA_x(MFe)_y]_5$ specimens blended with varying amounts of Sodium ascorbate and MFe.

Sample	LDPE (phr)	Sodium ascorbate (SA) (phr)	MFe (phr)
$L_{95}(MFe)_5$	100	0	10
$L_{95}[SA_1(MFe)_9]_5$	100	1	9
$L_{95}[SA_3(MFe)_7]_5$	100	3	7
$L_{95}[SA_5(MFe)_5]_5$	100	5	5
$L_{95}[SA_7(MFe)_3]_5$	100	7	3
$L_{95}[SA_9(MFe)_1]_5$	100	9	1
$L_{95}(SA)_5$	100	10	0

2.3 Morphology analysis

In order to understand the distribution of oxygen scavenger powders in the matrixes of LDPE film specimens, the oxygen absorbable LDPE specimens were observed using a HITACHI S-3000N scanning electron microscope (SEM). The specimens were gold-coated at 15Kev for 30 seconds before SEM examinations. The compositions on the surface of the film specimens were determined with a HORIBA 7201-H energy dispersive X-rays (EDX) equipped on the scanning electron microscope described above.

2.4 Oxygen depletion experiments

The film specimens used in each oxygen depletion experiments were prepared by sectioning the hot-pressed films prepared above into a rectangular slices with a dimension of 3 × 5 × 0.03 cm. A 300 ml conical flask filled with 200 ml of water was used for the oxygen depletion experiments. The slice specimens were hung on a thread, which was clamped on a conical flask by a sealing stopple. In contrast, 2 grams pure oxygen scavenger powders were heated at 150 oC for 1 minute. The heat-treated together with the pure oxygen scavenger powders without heat treatment were supported and wrapped by filter paper before hanging in conical flask and performing oxygen depletion experiment, respectively.

Under such circumstance, the relative humidity present in the airtight flask was controlled at 100% relative humidity.

The residual oxygen concentrations present in the conical flask were examined using a China 9800T Gas Chromatography instrument equipped with a thermal conductivity detector, which was purchased from Shanghai Kechuang Chromatograph Instruments Corporation, Shanghai, China. The column used for separation of nitrogen and oxygen contained in the conical flask has an inside diameter of 0.5 mm and a length of 2 m, wherein the column was packed with molecular sieves of 5Å (60-80mesh). Helium flowing at 15 ml/min was used as the carrier gas. The injection, column and detector temperature was set at 70, 100 and 90oC, respectively. All the oxygen depletion tests were carried out at 30 oC and 100% relative humidity for varying amounts of time.

2.5 Mechanical properties analysis

The tensile properties of the hot-pressed oxygen absorbable specimens were determined using a Shimadzu tensile testing machine model AG-10KNA at 28°C and a crosshead speed of 50 mm/min. A 35mm gauge length was used during each tensile experiment. The dimensions of the dog-bone shaped specimens were prepared according to ASTM D638 type IV standard. The values of tensile strength and elongation at break were obtained based on the average tensile results of at least five tensile specimens.

3 RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis

The thermogravimetric analysis (TGA) thermograms of pure ascorbic acid (Vc), sodium ascorbate (SA) powders and low density polyethylene (LDPE) are summarized in Fig. 1. As shown in Fig. 1, the weight loss of Vc powder starts at 185.7°C, and then increase abruptly at temperatures between 195.8 to 234.1 °C. The total weight loss percentage of the Vc powder reaches 15.0% as the temperature reaches 212.2 °C, at which the weight loss rates reach the maximum. The total weight loss percentage of Vc powder is 69.4% as the temperature reaches 500 °C. In contrast, the temperatures correspond to the initial and maximum rate of weight loss of SA are 212.4 and 230.8 °C, respectively, which are significantly higher than those of Vc powder. The total weight loss percentages of SA powder are 14.1% and 52.0% as the temperatures reach 230.8 and 500 °C, which are significantly lower than those of the Vc powder. These TGA results clearly suggest that the thermal stability of SA powder is significantly better than that of Vc powder. On the other hand, the temperatures correspond to the initial and maximum rate of weight loss of LDPE are 289.9 and 477.1 °C, respectively, which are significantly higher than those of Vc and SA powders. The weight loss percentage of LDPE specimen is nearly 100% as the temperature reaches 500°C.
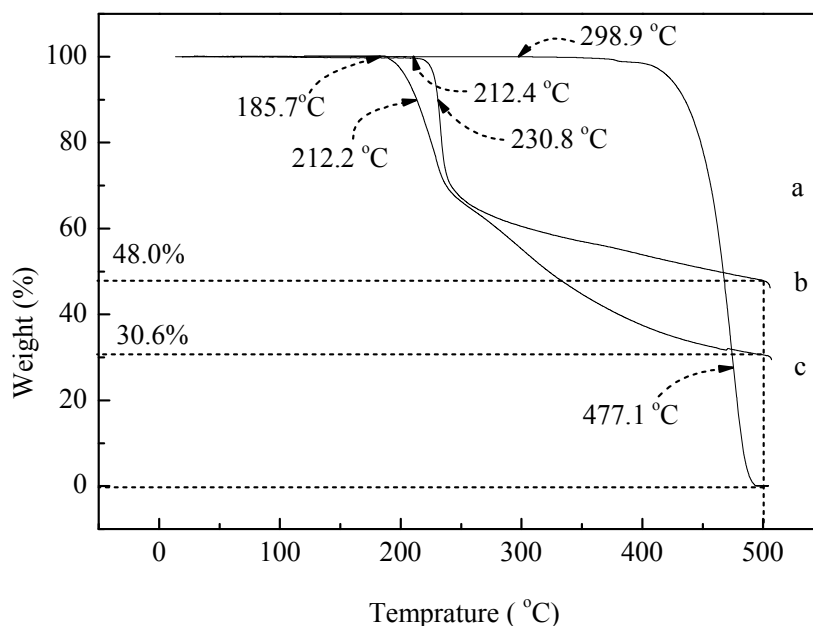

Figure 1 TGA thermograms of (a) LDPE, (b) ascorbic acid and (c) sodium ascorbate powders.

Fig. 2 summarized the TGA thermograms of $L_{95}(SA)_5$ and $L_{95}(Vc)_5$ specimens. After adding SA or Vc oxygen scavenger powders in LDPE resins, the temperatures of the initial weight loss of $L_{95}(SA)_5$ and $L_{95}(Vc)_5$ specimens reduce significantly from 212.4 and 185.7 °C to 145.5 and 54.6 °C, respectively. Similarly, the temperature corresponding to the maximum rate of weight loss of LDPE reduces significantly from 477.1 to 472.8 and 465.3 °C for $L_{95}(SA)_5$ and $L_{95}(Vc)_5$ specimens, respectively. In contrast, the temperatures corresponding to those maximum rate of weight loss of SA and Vc powders remain relatively the same (i.e. 233.8 and 211.2 °C) for $L_{95}(SA)_5$ and $L_{95}(Vc)_5$ specimens. These TGA results clearly suggest that the thermal stability of $L_{95}(SA)_5$ specimen is significantly higher than that of $L_{95}(Vc)_5$ specimen, but lower than that of pure LDPE. However, partially thermal or oxidized degradation of Vc and SA powders can occur during melt-blending processes of $L_{95}(SA)_5$ and $L_{95}(Vc)_5$ specimens, and hence, significantly reduce their thermal stability.
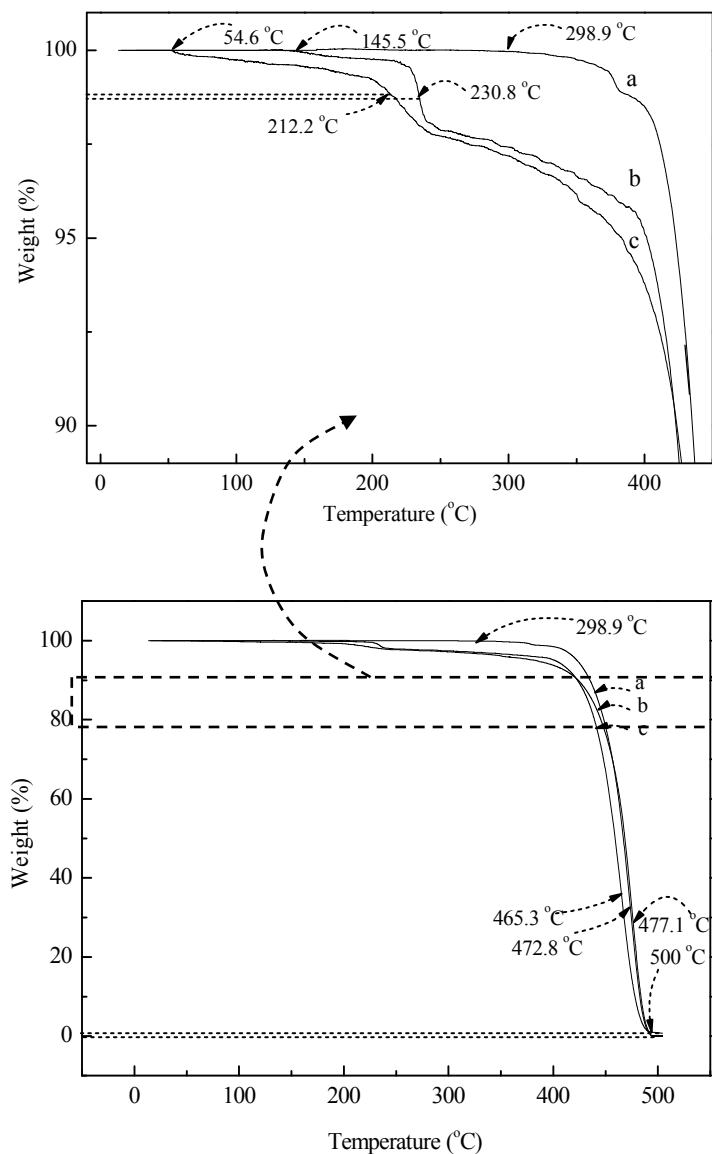

Figure 2 TGA thermograms of (a) LDPE, (b) $L_{95}(SA)_5$ and (c) $L_{95}(Vc)_5$ specimens.

3.2 Morphology and composition analysis of the oxygen scavengers filled LDPE specimens

Typical SEM micrographs and EDX analysis of the compositions on the surfaces of $L_{95}(Vc)_5$, $L_{95}(SA)_5$, $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ samples are summarized in Fig.3. As shown in Fig. 3, significantly aggregated Vc, SA, Fe and MFe powders were not fond in $L_{95}(Vc)_5$, $L_{95}(SA)_5$, $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ samples, respectively. However, the average particle sizes of Vc and SA powders are about 1 μm that are relatively smaller than those of the Fe (MFe) powders with original particle sizes of about 1 to 3 μm, respectively. In contrast, a thin, slightly transparent layer of NaCl was found covering the MFe but not the Fe powders. As expected, the EDX composition analysis of the MFe particles present on the surfaces of the $L_{95}(MFe)_5$ specimens indicates that the main compositions of the MFe particles are Na, Cl and Fe elements. Meanwhile, much more volume contents of Vc and SA powders were found on the $L_{95}(Vc)_5$ and $L_{95}(SA)_5$ series samples than those of the $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ series samples with the same weight loadings of Fe and MFe oxygen scavenger. Apparently, this is due to the density difference between the iron and Vc and SA powders (7.8 g/cm^3 v.s. 1.65g/cm^3 and 1.98g/cm^3).

Typical SEM micrographs and EDX analysis of the compositions on the surfaces of $L_{95}[Vc_xMFe_y]_5$ and $L_{95}[SA_xMFe_y]_5$ series samples are shown in Figs. 4 and 5. It is interesting to note that certain Vc powders were found surrounding but not over-wrapping on the surfaces of the MFe powders as the weight ratios of Vc to MFe present in the $L_{95}[Vc_xMFe_y]_5$ specimens are between 3/7 and 7/3 (see Figs. 4b to 4d). However, as shown in Figs. 4e, the MFe powders found in $L_{95}[Vc_xMFe_y]_5$ samples were nearly wrapped by the ascorbic acid powders as weight ratios of Vc to MFe are far more than 7/3 (i.e. $L_{95}[Vc_9MFe_1]_5$ specimen). Similar morphological characteristics were found in the $L_{95}[SA_xMFe_y]_5$ series samples, wherein the SA powders were found surrounding but not over-wrapping on the surfaces of the MFe powders with weight ratios of Vc to MFe are more than 5/5.

3.3 Oxygen depletion properties

The residual oxygen concentrations (O_{2r}) present in the airtight conical flasks of virgin and heat-treated Vc, SA, Fe and MFe oxygen scavengers are summarized in Fig. 6. As expected, the oxygen concentrations present in the airtight flasks of virgin and heat-treated Vc, SA, Fe and MFe oxygen scavengers reduce as the testing time increases. The oxygen depletion efficiency of MFe powder is significantly better than that of virgin Vc, SA and Fe powders. For instance, the O_{2r} values present in the airtight flask of the virgin MFe is 91.7% lower than that of Fe after 48 hours of oxygen removing experiments. As suggested in our previous investigations [26, 27], these interesting results are attributed to the fact that NaCl well known as an efficient catalyst for the oxidation of Fe powders can easily absorb water vapor and substantially disassociates into Na$^+$ and Cl$^-$ ions in the moisture-rich environment. Presumably, the substantially increased Na$^+$ and Cl$^-$ ions can enhance the conductivity of the NaCl and Fe contained electrolytes and trigger Fe oxygen scavenger to an active state for further oxidation reaction. It is, therefore, reasonable to infer that the oxygen depletion efficiency of MFe powder is much better than that of the Fe powder. In contrast, it is worth noting that the oxygen depletion efficiency of the virgin Vc powder is significantly better than that of the virgin SA and Fe powders. For instance, the O_{2r} values present in the airtight flask of the virgin Vc is 9.8%, which is lower than those of SA (i.e. 10.2%) after 48 hours of oxygen removing experiments. After heat treatment at 150°C for 1 minute, the oxygen depletion efficiency of the heat-treated Fe and MFe powders is about the same as those of the virgin Fe and MFe powders, respectively. In contrast, the oxygen depletion efficiency of the heat-treated Vc and SA powders is significantly worse than that of the corresponding virgin Vc and SA powders, respectively. In fact, as shown in Fig. 6, it is worth noting that the oxygen depletion efficiency of the heat-treated Vc powder is even worse than that of heat-treated SA powder. For instance, the O_{2r} values present in the airtight flask of the heat-treated SA are about 9.66% lower than those of the heat-treated Vc powder after 48 hours of oxygen removing experiments.

After adding the above oxygen scavengers in LDPE, the oxygen concentrations present in the airtight flasks of $L_{95}(Vc)_5$, $L_{95}(SA)_5$, $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ specimens reduce as the testing time increases (see Fig. 7). It is worth noting that the oxygen depletion efficiency of $L_{95}(SA)_5$ is significantly better than that of $L_{95}(Vc)_5$, $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ specimens. For instance, the O_{2r} value present in the airtight flask of $L_{95}(SA)_5$ specimen is 37.3% lower than that of $L_{95}(Vc)_5$ specimen after 48 days of oxygen removing experiments. As expected, the oxygen removal efficiency of Vc powder is significantly better than those of SA powder, since the molecular weight of Vc is significantly smaller than that of SA (176.13 vs. 216.12g/mol) and both Vc and SA molecules have two same hydroxyl groups to remove oxygen molecules during their oxygen removal experiments. However, as evidenced by TGA, the thermal stability of SA powder is significantly better than Vc powder. It is reasonable to infer that the oxygen depletion properties of heat-treated SA powders present in $L_{95}(SA)_5$ specimen are significantly better than heat-treated Vc powders in $L_{95}(Vc)_5$ specimen. On the
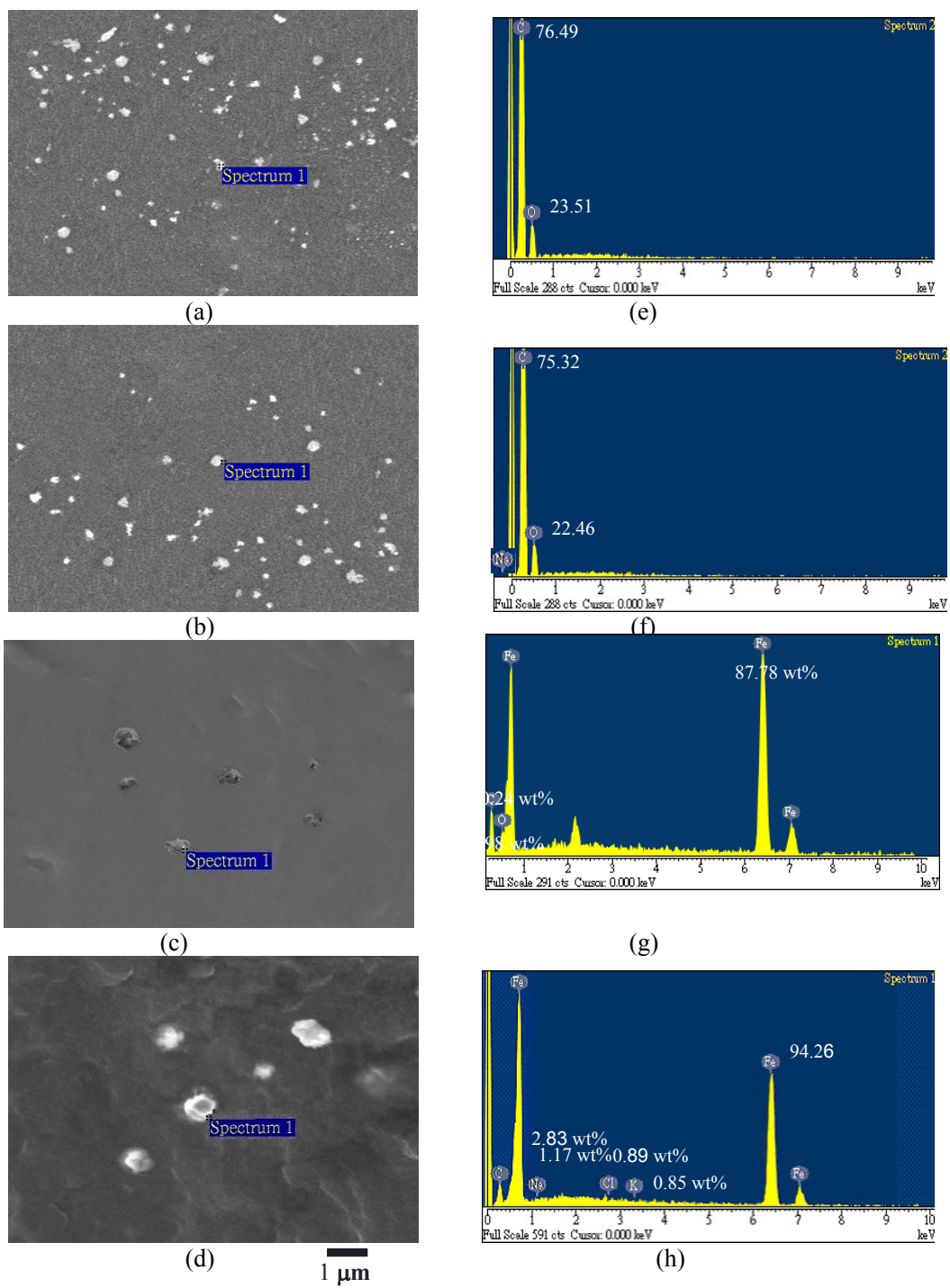
Figure 3   SEM micrographs of the fracture surfaces and EDX composition analysis of the particles present in (a) $L_{95}(Vc)_5$, (b) $L_{95}(SA)_5$, (c) $L_{95}(Fe)_5$, (d) $L_{95}(MFe)_5$ specimens.
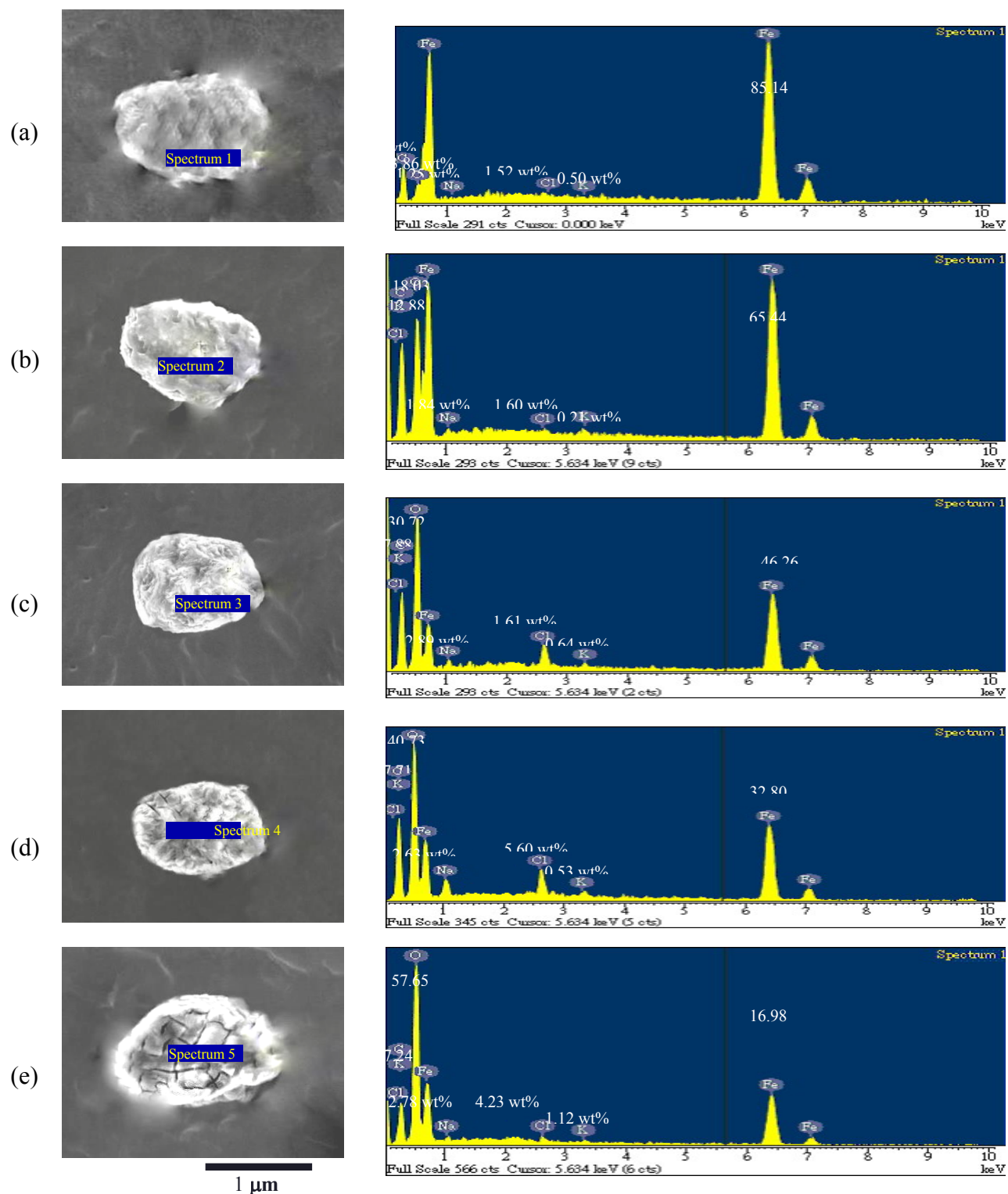
Figure 4 SEM micrographs of the fracture surfaces and EDX composition analysis of the particles present in (a) $L_{95}[Vc_1(MFe)_9]_5$, (b) $L_{95}[Vc_3(MFe)_5]_7$, (c) $L_{95}[Vc_5(MFe)_5]_5$, (d) $L_{95}[Vc_7(MFe)_3]_5$ and (e) $L_{95}[Vc_9(MFe)_1]_5$ film specimens.
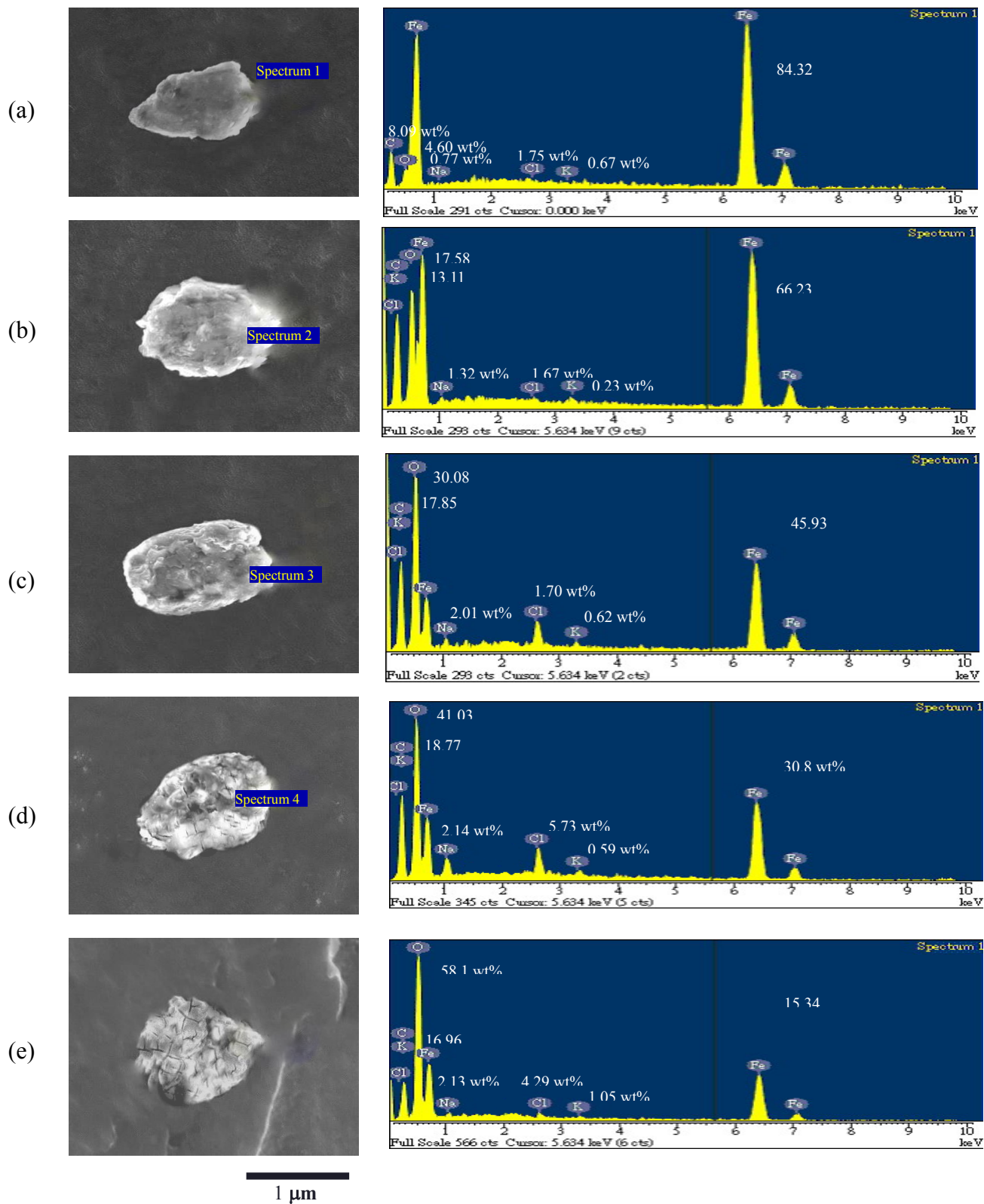
Figure 5 SEM micrographs of the fracture surfaces and EDX composition analysis of the particles present in (a) $L_{95}[SA_1(MFe)_9]_5$, (b) $L_{95}[SA_5(MFe)_5]_5$, (c) $L_{95}[SA_5(MFe)_5]_5$, (d) $L_{95}[SA_7(MFe)_3]_5$ and (e) $L_{95}[SA_9(MFe)_1]_5$ film specimens.
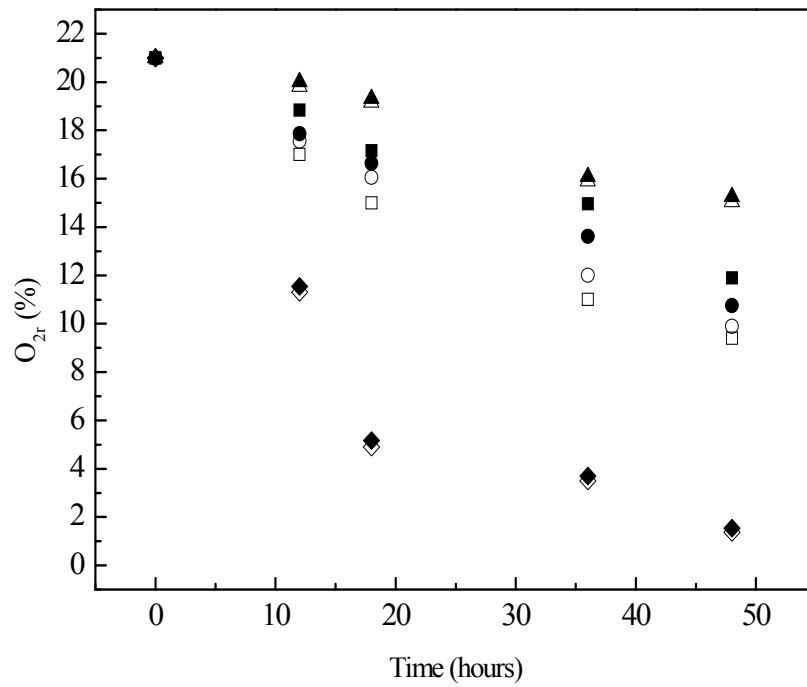
Figure 6 The residual oxygen concentrations (O_{2r}) present in the airtight conical flasks of virgin Vc ($\square$), SA ($\circ$), Fe ( ) and MFe ($\diamond$) oxygen scavengers and heat-treated Vc ($\blacksquare$), SA ($\bullet$), Fe($\blacktriangle$) and MFe ($\blacklozenge$) oxygen scavengers.
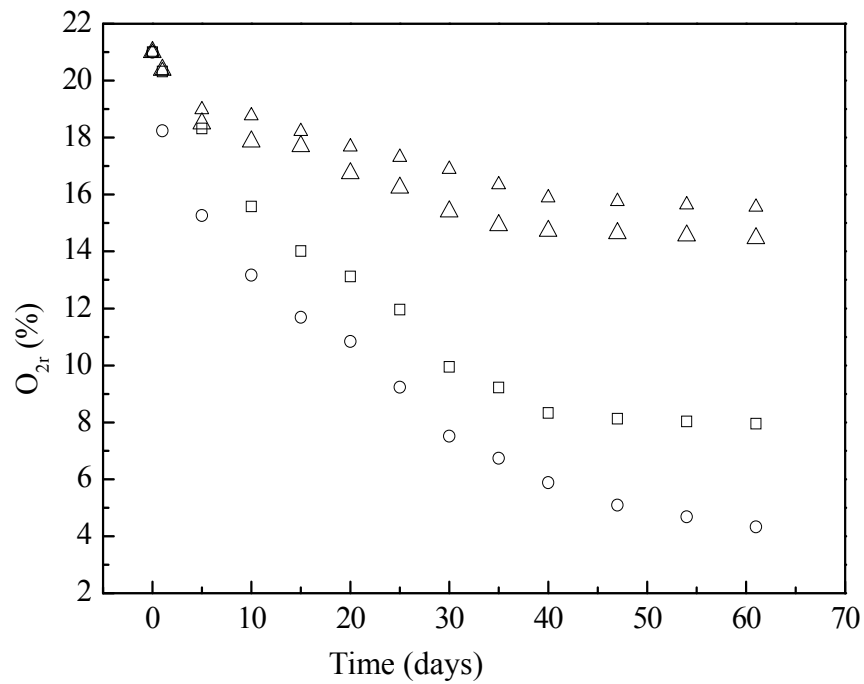

Figure 7 Residual oxygen concentrations (O_{2r}) present in the airtight conical flasks

of $L_{95}(Vc)_5$($\square$), $L_{95}(SA)_5$($\circ$), $L_{95}(Fe)_5$( ) and $L_{95}(MFe)_5$( ) specimens.

other hand, as reported in our previous investigations [26, 27], the oxidation of MFe and/or Fe powders can perform at fast rates only in a moisture-rich environment. It is, therefore, reasonable to understand that poorer oxygen depletion efficiency can be found in $L_{95}(MFe)_5$ and $L_{95}(MFe)_5$ specimens as compared to that of the $L_{95}(SA)_5$ specimen, since the MFe and/or Fe powders are buried in a moisture-poor environment of LDPE resins.

Figs. 8 and 9 summarized the oxygen depletion properties of the $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples, in which Vc/MFe or SA/MFe oxygen scavenger compounds were melt-blended in the LDPE resins. As expected, the oxygen concentrations present in the airtight flasks of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series specimens reduce as the testing time increases.   At a fixed weight ratio of Vc/SA to MFe of the oxygen scavenger compounds, the oxygen depletion efficiency of $L_{95}[SA_x(MFe)_y]_5$ series specimens is significantly better than that of $L_{95}[Vc_x(MFe)_y]_5$ series specimens. For instance, the O_{2r} values present in the airtight flask of $L_{95}[SA_5(MFe)_5]_5$ is 8.9% lower than that of $L_{95}[Vc_5(MFe)_5]_5$ after 30 days of oxygen removing experiments. It is worth noting that the oxygen depletion efficiency of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples increase initially as the weight ratios of Vc/MFe or SA/MFe increase. In fact, at weight ratios of Vc/MFe and SA/MFe higher than 3/7 and 5/5, respectively, the O_{2r} values present in the airtight flask of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples at any time are even lower than those of the $L_{95}(Vc)_5$ and $L_{95}(SA)_5$ specimens, respectively. The oxygen depletion efficiency of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ specimens is the best as the weight ratios of Vc/MFe and SA/MFe reach 7/3 and 9/1, respectively.
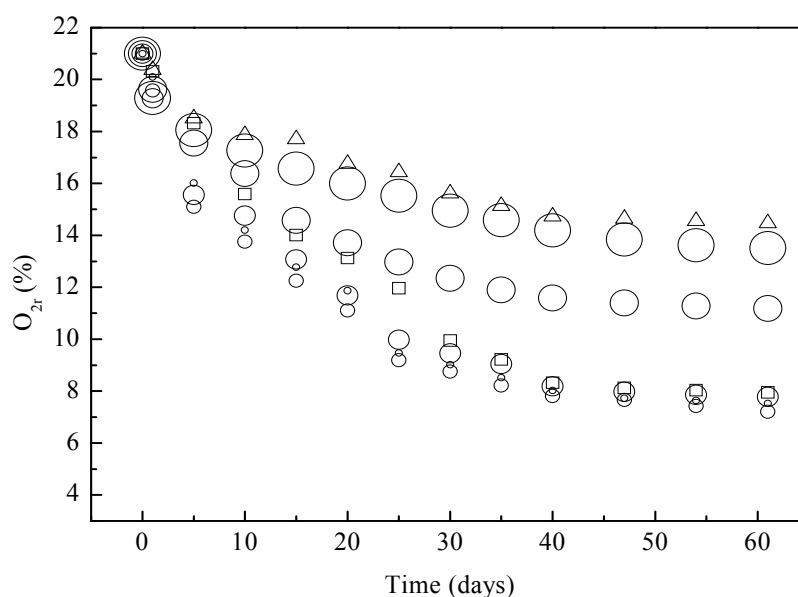

Figure 8 Residual oxygen concentrations (O_{2r}) present in the airtight conical flasks of $L_{95}(MFe)_5$( ), $L_{95}[Vc_1(MFe)_9]_5$(○), $L_{95}[Vc_3(MFe)_7]_5$(○), $L_{95}[Vc_5(MFe)_5]_5$(○), $L_{95}[Vc_7(MFe)_3]_5$(○), $L_{95}[Vc_9(MFe)_1]_5$(○) and $L_{95}(Vc)_5$(□) specimens.

As reported by Miller and Buettner [28], the Fe^{2+} ions generated during the oxidation process of Fe powders can serve as an effective catalyst for Vc and SA to remove oxygen, wherein the Vc and SA are oxidized by oxygen and transformed into water and dehydroascorbic acid and/or dehydroascorbate. However, as mentioned above, poor oxygen depletion efficiency was found in $L_{95}(MFe)_5$ and $L_{95}(MFe)_5$ specimens, since MFe and/or Fe powders were buried in a moisture-poor environment of LDPE resins. Presumably, the water released after the oxidation of Vc and SA can make MFe present in a moisture-rich environment, in which NaCl can easily absorb water vapor, substantially disassociates into Na^+ and Cl^- ions, enhance the conductivity of the NaCl and Fe contained electrolytes and trigger Fe oxygen scavenger to an active state for further oxidation reaction. Furthermore, the Fe^{2+} ions generated during the oxidation process of Fe powders can further serve as an effective catalyst for Vc and SA to remove oxygen.
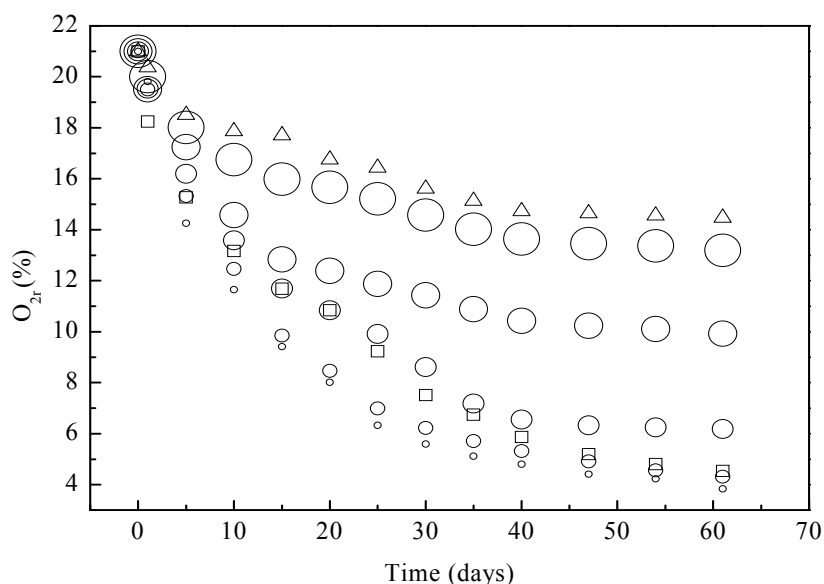
Figure 9 Residual oxygen concentrations (O_{2r}) present in the airtight conical flasks of $L_{95}(MFe)_5$ ( ), $L_{95}[SA_1(MFe)_9]_5$ (○), $L_{95}[SA_3(MFe)_7]_5$ (○), $L_{95}[SA_5(MFe)_5]_5$ (○), $L_{95}[SA_7(MFe)_3]_5$ (○), $L_{95}[SA_9(MFe)_1]_5$ (○) and $L_{95}(SA)_5$ (□) specimens.

As shown in the previous section, certain Vc powders were found surrounding but not over-wrapping on the surfaces of the MFe powders as the weight ratios of Vc to MFe present in the $L_{95}[Vc_xMFe_y]_5$ specimens are between 3/7 and 7/3. Presumably, the "synergistic" oxygen depletion properties of the oxygen-scavenging plastic film samples are attributed to the "catalytic effect" caused by the optimum amounts of water molecules and Fe^{2+} ions formed during the oxidation processes of Fe and Vc powders.   On the other hand, the MFe powders found in the $L_{95}[Vc_x(MFe)_y]_5$ specimen were nearly wrapped by the ascorbic acid powders as the weight ratio of Vc/MFe is more than 7/3. The oxygen depletion properties of the over-wrapped MFe powders can be significantly inhibited (i.e. $L_{95}[Vc_9(MFe)_1]_5$), since the MFe powders are barely exposed to the oxygen and water molecules and can not play as an effective oxygen scavenger. Under such circumstances, the amounts of Fe^{2+} ions generated may not be enough to serve as an effective catalyst for the oxidation of ascorbic acid powders.   It is, therefore, reasonable to believe that at weight ratios of Vc/MFe higher than 3/7, the O_{2r} values present in the airtight flask of $L_{95}[Vc_x(MFe)_y]_5$ series samples at any time are even lower than those of the $L_{95}(Vc)_5$ specimens. Moreover, the oxygen depletion efficiency of $L_{95}[Vc_x(MFe)_y]_5$ specimens is the best as the weight ratios of Vc/MFe reach 7/3.   By the same analogy, it is reasonable to infer that at weight ratios of SA/MFe higher than 5/5, the O_{2r} values present in the airtight flask of $L_{95}[SA_x(MFe)_y]_5$ series samples at any time are even lower than those of the $L_{95}(SA)_5$ specimens.   Moreover, the oxygen depletion efficiency of $L_{95}[SA_x(MFe)_y]_5$ specimens is the best as the weight ratios of SA/MFe reach 9/1.

3.4 Mechanical properties

The tensile properties of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples are summarized in Fig. 10. It is worth noting that the values of tensile strengths (σ_f) and elongations at break (ε_f) of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples increase significantly as their MFe loadings of oxygen scavenger compounds increase, respectively. For instance, the σ_f and ε_f values of $L_{95}[SA_x(MFe)_y]_5$ series samples increase from 9.2MPa / 46.0% to 11.2MPa / 74.3%, as the weight ratios of SA to MFe in the oxygen scavenger compounds reduce from 9/1 to 1/9. In fact, the σ_f and ε_f values of $L_{95}[SA_x(MFe)_y]_5$ series samples are higher than those of   the corresponding $L_{95}[Vc_x(MFe)_y]_5$ series samples with the same loadings of oxygen scavenger compounds, respectively. For instance, the σ_f and ε_f values of the $L_{95}[SA_5(MFe)_5]_5$ are about 2.6% and 5.1% higher than those of the $L_{95}[Vc_5(MFe)_5]_5$ specimen, respectively.
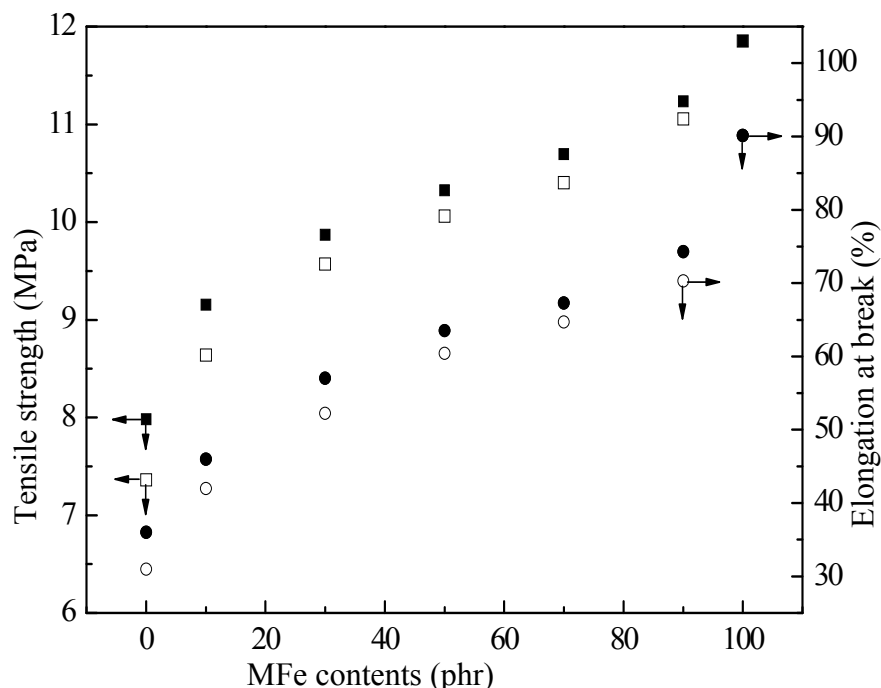
Figure 10 Tensile strength and elongation at break of $L_{95}[Vc_x(MFe)_y]_5$ ($\square$, $\circ$) and $L_{95}[SA_x(MFe)_y]_5$ ($\blacksquare$, $\bullet$) specimens.

Presumably, during the tensile experiments of the oxygen scavenger compounds filled LDPE specimens, the presence of oxygen scavenger powers can cause "stress concentration" and "early breakage of LDPE molecules" at the boundaries between oxygen scavenger powders and the LDPE resins, since the interfacial adhesion between the scavenger powders and LDPE resins is poor. The degree of "stress concentration" and "early breakage of LDPE molecules" at the boundaries is expected to reduce as the volumes of the oxygen scavenger compounds reduce. However, the density of the iron powders (i.e. 7.8 g/cm^3) is much higher than that of the Vc (i.e. 1.65g/cm^3) and SA (i.e. 1.98g/cm^3) powders. The volumes of the Fe and MFe powders are much smaller than those of Vc and SA powders with the same weights. By the same analogy, the volumes of 5 phr oxygen scavenger compounds present in the $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples can reduce significantly as their MFe contents present in the oxygen scavenger compounds increase, respectively. As a consequence, the σ_f and ε_f values of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples increase significantly as their MFe contents present in the oxygen scavenger compounds increase, respectively. By the same analogy, it is reasonable to infer that σ_f and ε_f values of $L_{95}[SA_x(MFe)_y]_5$ series samples are higher than those of corresponding $L_{95}[Vc_x(MFe)_y]_5$ series samples with the same MFe oxygen scavenger contents, since the density of SA is higher than that of Vc.

4 CONCLUSIONS

The thermal stability, oxygen depletion and tensile properties of low density polyethylene (LDPE) resins filled with ascorbic acid (Vc), sodium ascorbate (SA), iron (Fe) and modified iron (MFe) oxygen scavengers were systematically investigated. TGA results clearly suggest that the thermal stability of SA powder and $L_{95}(SA)_5$ specimen is significantly better than that of Vc powder and $L_{95}(Vc)_5$ specimen, respectively. The oxygen depletion efficiency of $L_{95}(SA)_5$ is significantly better than that of $L_{95}(Vc)_5$, $L_{95}(Fe)_5$ and $L_{95}(MFe)_5$ specimens, although the virgin SA powders exhibit worse oxygen depletion efficiency than Vc, Fe or MFe powders before melt blending. Moreover, at a fixed weight ratio of Vc (or SA) to MFe of the oxygen scavenger compounds, the oxygen depletion efficiency of $L_{95}[SA_x(MFe)_y]_5$ series specimens is always significantly better than that of $L_{95}[Vc_x(MFe)_y]_5$ series specimens, wherein the oxygen depletion efficiency of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ specimens reach the best as the weight ratios of Vc/MFe and SA/MFe is 7/3 and 9/1, respectively. In fact, at weight ratios of Vc/MFe and SA/MFe higher than 3/7 and 5/5, respectively, the residual oxygen concentration values present in the airtight flask of $L_{95}[Vc_x(MFe)_y]_5$ and

$L_{95}[SA_x(MFe)_y]_5$ series samples at any time are even lower than those of the $L_{95}(Vc)_5$ and $L_{95}(SA)_5$ specimens, respectively.

Further SEM and EDX analysis of the compositions on the surfaces of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series specimens indicate that Vc and SA powders were found surrounding but not over-wrapping on the surfaces of the MFe powders as the weight ratios of Vc/MFe and SA/MFe are between 3/7 and 7/3 and higher than 5/5, respectively.   On the other hand, the MFe powders found in the $L_{95}[Vc_x(MFe)_y]_5$ specimens were nearly wrapped by the Vc powders as the weight ratios of Vc to MFe are more than 7/3.   Presumably, the oxygen depletion properties of MFe powders can be significantly inhibited after they were over-wrapped, since oxygen and water molecules can no longer enter into the over-wrapped MFe powders easily, which can not only reduce the inherent oxygen depletion properties of MFe powders but also can inhibit the oxygen depletion properties of Vc and SA powders without releasing the catalytic Fe^{2+} from MFe powders.

The σ_f and ε_f of $L_{95}[Vc_x(MFe)_y]_5$ and $L_{95}[SA_x(MFe)_y]_5$ series samples increase significantly as their MFe loadings of oxygen scavenger compounds increase, respectively. In fact, the σ_f and ε_f values of $L_{95}[SA_x(MFe)_y]_5$ series samples are higher than those of the corresponding $L_{95}[Vc_x(MFe)_y]_5$ series samples with the same loadings of oxygen scavenger compounds, respectively.   Apparently, this is due to the fact that the volumes of the MFe powders are much smaller than those of the Vc and SA powders with the same weight loadings, wherein the volumes of SA powder is much smaller than that of Vc powder with the same weight loadings.

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