Influence of $\cdot\text{OH}$ Radicals on the Radiation Effect of Polydimethylsiloxane Latex^{*}

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Abstract By measuring the gel fraction and GPC spectra of irradiated polydimethylsiloxane (PDMS) samples, the radiation effect of PDMS in latex form was investigated. Results showed that the $\cdot\text{OH}$ radical could not only initiate the radiation crosslinking of PDMS latex, but also accelerate the scission of PDMS molecular chain. For the PDMS latex without additives, the effect of $\cdot\text{OH}$ on the crosslinking behavior is not obvious. However, the addition of H_2O_2 or KIO_4 or N_2O which could increase the concentration of $\cdot\text{OH}$ would enhance the radiation degradation of PDMS. Moreover, with the increase of absorbed dose, the degradation is more predominant to lead to the drop of gel fraction. Particularly, in the presence of crosslinking sensitizer-trimethylol propane trimethacrylate (TMPTMA), when the dose was above 40 kGy, the excess $\cdot\text{OH}$ radical accelerated remarkably the degradation of PDMS chain which resulted in the narrow polydispersity of molecular weight and increase in content of PDMS with low molecular weight, and decrease of gel fraction, comparing with those of irradiated PDMS latex without TMPTMA. This suggested that the synergetic interaction perhaps existed between TMPTMA and excess $\cdot\text{OH}$ radical. This might be attributed to that the $\cdot\text{OH}$ radicals react with TMPTMA firstly, the resulted product might accelerate the degradation of PDMS.

Keywords: Hydroxyl radical, Polydimethylsiloxane latex, Radiation crosslinking, Radiation degradation, Crosslinking sensitizer

Comparing with the radiation vulcanization of bulk rubber, the radiation vulcanization of rubber latex has many advantages such as fast crosslinking, low absorbed dose and weak degradation and good stability. In addition, we have found that the size of rubber particles in latex could be fixed by gamma-induced crosslinking reaction, then combining with spray drying method^[1], the ultra-fine powdered rubber could be produced easily. Moreover, these ultra-fine powdered rubber can be used as effective impact modifier in thermoplastic and thermoset plastic^[2-4], or thermoplastic elastomer^[5].

Polydimethylsiloxane (PDMS) possesses a number of special properties, such as high flexibility and thermostability, excellent weather and chemical resistance and good biological compatibility. Many literatures about the radiation crosslinking of PDMS in solid state have been reported because of its unique

configuration properties^[6-10], however, few papers are related to the radiation crosslinking of PDMS in latex form. In order to produce the ultra-fine powdered PDMS rubber, it is necessary to study the radiation crosslinking behavior and crosslinking mechanism of PDMS latex. Our previous paper^[11] has reported the influences of many factors such as dose, dose rate, and atmosphere, polyfunctional monomer on the radiation crosslinking of PDMS latex. Due to the existence of liquid water in PDMS latex, the products in gamma radiolysis of water will probably affect the radiation crosslinking reaction of PDMS molecular chain. Because $\cdot\text{OH}$ radical is the predominant primary product in the gamma radiolysis of water, it is necessary to investigate the effect of $\cdot\text{OH}$ radical on the radiation of PDMS.

1 Experimental

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1.1 Materials

The commercial PDMS rubber latex was used in this work. The M_n and M_w of PDMS are 1.20×10^5 , 1.91×10^5 respectively, which were determined by using GPC. The dry rubber content of PDMS latex is 30%.

Trimethylol propane trimethacrylate(TMPTMA) with three double bonds in each monomer was used as crosslinking sensitizer in this study. Other reagents were obtained commercially.

1.2 Irradiation

After adding the crosslinking sensitizer to the latex, the mixture was strongly stirred for 1 h and irradiated by γ -rays at room temperature. The dose rate was determined by a Fricke dosimeter.

1.3 The measurement of gel fraction

The irradiated latex was casted on a glass plate to obtain a dried rubber film at room temperature. Then the resulted film was dried under vacuum at 50~60 °C to a constant weight. The dry films were extracted with toluene in Soxhlet extractor for 24 h in the presence of some antioxidant. The insoluble residue was dried to a constant weight in vacuum oven at 50~60 °C. Finally the gel fraction was determined by weighing.

1.4 GPC analysis

The dry rubber film was extracted with water in Soxhlet extractor to eliminate the surfactant and other water-soluble impurities before measurement of GPC. The molecular weight of PDMS rubber film was recorded by using GPC with a Waters Styragel HT4 chromatograph column.

2 Results and discussion

When dilute aqueous solution of a polymer is subjected to γ -rays or fast electrons, the energy of ionizing radiation is primarily absorbed by water. As a result, reactive intermediates are formed, mainly OH radicals, H-atoms and hydrated electrons.

It is well known that $\cdot\text{OH}$ could react with a number of polymers by hydrogen abstraction to produce macromolecular radicals. In addition, it could initiate various reaction of polymer such as scissions of polymer chain, the disproportionation of macromolecular radicals, which is determined by the chemical structure of the polymer^[12]. Due to the low G value (which refers to the number of molecules formed on irradiation per 100 eV

energy absorbed) of $\cdot\text{OH}$ in the radiolysis of water ($G_{\cdot\text{OH}}=2.7$), we added some reagents into PDMS latex to produce more $\cdot\text{OH}$ radicals in order to study clearly the effect of $\cdot\text{OH}$ on the crosslinking behavior of PDMS latex.

2.1 Effect of $\cdot\text{OH}$ on the radiation crosslinking of PDMS latex without crosslinking sensitizer

In the experiment, 1% H_2O_2 (w/w of PDMS) were added into the PDMS latex and the samples were irradiated under different absorbed doses. Fig.1 shows that there is a slight effect of addition of H_2O_2 on the gel fraction of PDMS latices at low dose (R), while, at dose beyond 60 kGy, the gel fraction of PDMS with 1% H_2O_2 is less than that of PDMS without additives. In order to study the radiation effect on PDMS latices, we measured the molecular weight and its distribution of sol in irradiated PDMS samples before gelation by using GPC. Fig.2 gives the GPC chromatogram of sol in irradiated PDMS latices without additives and with 1% H_2O_2 at 10 kGy (below gelation dose), respectively. After the addition of 1% H_2O_2 , no marked changes could be found for the size of high molecular weight, moreover, the M_w of two PDMS samples are 2.31×10^5 and 2.40×10^5 , respectively, which is higher than unirradiated PDMS samples (1.91×10^5). It indicates that the PDMS chain in latex could be intermolecular crosslinked under gamma irradiation^[12], and $\cdot\text{OH}$ as active particles resulted from the radiolysis of H_2O_2 could also initiate the crosslinking reaction of PDMS. However, it can be noted that the ratio of peak area of low molecular weight to high molecular weight of irradiated PDMS latices increased from 0.049 to 0.093 in the presence of H_2O_2 . This might be attributed to promotion of the irradiation degradation

Fig.1 Relationship between gel fraction and absorbed dose(R) for γ -ray irradiated PDMS latex with or without H_2O_2

1) without additives; 2) 1% H_2O_2

Fig.2 The GPC chromatogram of irradiated PDMS

latex samples(absorbed dose 10 kGy)

a) without additives, peak 1: $M_n=143979$, $M_w=230971$, polydispersity: 1.60; peak 2: $M_n=3727$, $M_w=3996$, polydispersity: 1.07;

b) with 1% H_2O_2 , peak 1': $M_n=168677$, $M_w=239640$, polydispersity: 1.42; peak 2': $M_n=6966$, $M_w=7281$, polydispersity: 1.05

of PDMS chain to some extent by the excess $\cdot\text{OH}$ radical. The possible reason might be that $\cdot\text{OH}$ could attack the main chain of PDMS in the interface between water and PDMS particles and lead to the scission of macromolecular chain. With the increase of absorbed dose, the acceleration to the degradation of PDMS by H_2O_2 is more obvious; consequently, the gel fraction was reduced after adding 1% H_2O_2 at dose above 60 kGy. The similar results are also reported by Alam^[13], he found that PDMS rubber particles in solid could be hydrolysed in the presence of water by gamma irradiation under sealing storage for 15 days, furthermore, he observed that characteristic peaks for $\text{Si}-\text{O}-\text{Si}$ bond and $\text{Si}-\text{OH}$ bonding appeared in the ^{17}O -NMR spectrum,

Fig.3 The effect of H_2O_2 on the crosslinking behavior of γ -ray irradiated PDMS latex

thus, it indicated that $\cdot\text{OH}$ could react with PDMS and accelerate the scission of PDMS main chain.

2.2 Effect of $\cdot\text{OH}$ on radiation crosslinking of PDMS latex in the presence of crosslinking sensitizer

In this study, three methods have been used to increase the amount of $\cdot\text{OH}$ radicals in radiolysis of water. The possible reactions are given as follows:

Fig.3 shows the relationship of gel fraction and absorbed dose for PDMS samples with 1% TMPTMA, 1% H_2O_2 + 1% TMPTMA, 1% H_2O_2 , respectively. In the presence of TMPTMA, the gel fraction of PDMS latices with addition of 1% H_2O_2 decreased significantly in the studied dose range, comparing with those of PDMS latices without H_2O_2 . Although the using of 1% TMPTMA sensitizer could reduce the gelation dose from 30 kGy to 12.5 kGy^[11], the addition of H_2O_2 reduced distinctly the gel fraction of PDMS latices. Moreover, at the dose above 40 kGy, the gel fraction for PDMS with 1% TMPTMA+1% H_2O_2 is lower than irradiated PDMS sample with 1% H_2O_2 . Fig.4 also confirmed that addition of N_2O and KIO_4 could suppress the radiation crosslinking of PDMS. These results identify that excess $\cdot\text{OH}$ radical could indeed accelerate the degradation of PDMS at certain conditions. In addition, there is a synergetic interaction between TMPTMA and $\cdot\text{OH}$ radical. Clemens^[14] reported that the rate of reaction of $\cdot\text{OH}$ with a polymer is generally much

Fig.4 The effect of KIO_4 and N_2O on the crosslinking behavior of γ -ray irradiated PDMS latex (with 1% TMPTMA)

1) in air; 2) in N_2O ; 3) with 1% KIO_4

Fig.5 The GPC chromatogram of irradiated PDMS latex samples (absorbed dose 5.25 kGy)

a) with 1% TMPTMA, peak 1: $M_n=165898$, $M_w=236014$, polydispersity: 1.42; peak 2: $M_n=714$, $M_w=739$, polydispersity: 1.03;

b) with 1% TMPTMA+1% H_2O_2 , peak 1: $M_n=163513$, $M_w=224741$, polydispersity: 1.37; peak 2: $M_n=697$, $M_w=719$, polydispersity: 1.03

lower than that of the low-molecular-weight compound, therefore, $\cdot OH$ radical might react with TMPTMA firstly, which may prevent the improvement of TMPTMA for the crosslinking of PDMS, then, the existence of these impurities perhaps accelerate the degradation of PDMS.

On the other hand, the M_w and its distribution of irradiated PDMS without and with H_2O_2 in the presence of TMPTMA at low dose were determined by GPC. The results are demonstrated in Fig.5. It can be seen that the effect of excess $\cdot OH$ radical on size of high molecular weight could be negligible at dose of 5.25 kGy, the M_w of PDMS without H_2O_2 and with H_2O_2 are 2.36×10^5 and 2.25×10^5 respectively, whereas, the polydispersity of M_w of PDMS with H_2O_2 is much narrower than that without H_2O_2 . However, comparing the ratio of peak area of low M_w to that of high M_w , the latter is higher than the former, which are 0.51 and 0.58, respectively. It indicates that the molecular chains of PDMS have been broken, the content of low M_w increased after addition of H_2O_2 . In the previous study, we have analyzed the relationship between gel fraction and absorbed dose for irradiated PDMS latex with crosslinking sensitizer by using Charlesby-Pinner equation^[11], and we found that addition of crosslinking sensitizer could promote not only the crosslinking but also degradation. Increasing the content of $\cdot OH$ radicals would have some synergetic interaction with crosslinking sensitizer, therefore, the gel fraction was decreased significantly.

3 Conclusion

The $\cdot OH$ radicals as active species in the radiolysis of water have different effects on the crosslinking behavior of PDMS latex under different conditions. Usually, at low dose,

increase of $\cdot OH$ radical content could initiate the crosslinking of PDMS latex without crosslinking sensitizer, whereas the degradation of PDMS could be accelerated by excess $\cdot OH$ at dose beyond 60 kGy. Generally, the content of $\cdot OH$ is relatively low in PDMS latex during irradiation, therefore, the effect of $\cdot OH$ on the crosslinking property of PDMS latex could be ignored. However, if we added some additives which would increase the concentration of $\cdot OH$, the gel fraction of PDMS latex would be reduced remarkably, particularly, the irradiation degradation would be enhanced for the PDMS sample in the presence of TMPTMA, in spite of the fact that the addition of TMPTMA could reduce the gelation dose of PDMS latex. It demonstrated that $\cdot OH$ would have some synergetic interaction with TMPTMA, which might due to the special structure of PDMS and reaction activity of crosslinking sensitizer and $\cdot OH$ radicals.

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$\cdot\text{OH}$ 对聚二甲基硅氧烷乳液辐射效应的影响^{*}

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摘要 通过凝胶和溶胶分析与分子量测定的方法,研究了不同体系下, $\cdot\text{OH}$ 对 PDMS 乳液 γ 辐射效应的影响. 结果表明, $\cdot\text{OH}$ 不仅可引发聚二甲基硅氧烷的分子间交联,也能促进其降解. 对于纯 PDMS 乳液,在所研究的剂量范围内, $\cdot\text{OH}$ 对其辐射交联行为影响较小. 但若体系中加入 H_2O_2 、 KIO_4 和 N_2O 这些提高 $\cdot\text{OH}$ 生成产额的添加剂时, $\cdot\text{OH}$ 对 PDMS 的促降解作用会随着吸收剂量增加而表现更明显,导致凝胶含量与纯乳液辐照情况相比下降较多. 即使加入交联剂-三羟甲基丙烷三甲基丙烯酸酯(TMPTMA),在过量的 $\cdot\text{OH}$ 存在下,当吸收剂量大于 40 kGy 以上时, TMPTMA 不仅没有提高交联度,反而会与 $\cdot\text{OH}$ 协同,使 PDMS 的凝胶含量下降更显著,同时产生更多的小分子聚合物,并使 PDMS 的平均分子量分布变窄. 这可能是由于交联剂首先与 $\cdot\text{OH}$ 作用,形成的产物会加快 PDMS 的降解.

关键词: OH 自由基, 聚二甲基硅氧烷(PDMS)乳液, 辐射交联, 辐射降解, 交联剂

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