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Improved thermal stability of crosslinked PTFE using fluorine gas treatment

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ABSTRACT

Crosslinked PTFE (XF) samples were fluorinated at 293–593 K under 0.7–101 kPa F_2 and for 1 h to 7 days to improve its thermal stability. Because the weight uptake which may be caused by the fluorine addition was detected at room temperature, C=C bonds in XF can be fluorinated and the fluorine content was saturated after 72 h. Weights of all samples increased more than that of original XF through additional fluorination of C=C bonds, whereas it decreased by the chain-scission to form gaseous fluorocarbons such as CF_4. The intensity ratio in IR spectra of the peaks correspond to the double bond ($-CF=CF_2$) at 1785 cm^{-1} and the characteristic peaks of PTFE at 1794 cm^{-1}, I_{PTFE}/I_{PTFE} was smaller for the fluorinated XF rather than that for XF. Average values of heat of crystallization (ΔH_c) for all fluorinated XF samples were about 2 J/g higher than that of the original XF. The decomposition temperature calculated from the TG curves increased with increasing reaction temperature and reaction time up to 72 h. Thermal stability of XF was improved through fluorine gas treatment.

1. Introduction

Polytetrafluoroethylene (PTFE), $(-CF_2-CF_2-)_n$ is an important material for various industrial applications because of its many excellent properties: high resistivity, high thermal and chemical stability, low surface energy, potential biocompatibility, and so on. However, its high sensitivity to radiation is well known to limit its use in many applications, especially nuclear and space applications. Molecular weight decreases through chain-scission even if the amount of radiation is a small dose (e.g. several kiloGrays) and mechanical properties are degraded [1]. Radiation effects on PTFE have been studied extensively [2–10]. When PTFE is irradiated, the chain-end free radicals $(-CF_2-CF_2)$ and chain alkyl radicals $(-CF_2-CF-CF_2-)$ has been detected by using ESR. Among these radicals, the chain end radicals were main products of a chain scission [11]. Recently, Tabata and co-workers reported experimental evidence demonstrating network formation. Electron beam (EB) irradiation around the molten state (613 K) under oxygen-free atmosphere confirmed crosslinking of PTFE (XF). Irradiation against PTFE in the melt also confirmed the formation of CF_3 branches and double bonds between carbons [12–17]. This fact suggests that the thermal stability of PTFE modified by radiation is reduced in comparison to that of original PTFE. Both the melting point and decomposition point of XF were lower than those of original PTFE [18], probably because of the decrease of the crystal size that occurs by the chain-scission. This study shows that C=C lowers the thermal stability as it is converted into saturated bonds through fluorination.

2. Results and discussion

Table 1 lists reaction conditions of crosslinked PTFE (i.e. XF). Fig. 1 shows the relationship between weight change and reaction temperature under 51 kPa F_2 for 24 h. Sample weights were increased through fluorination. The weight increase of XF-A was greater than those of XF-B–XF-E. Weights of all samples increased more than that of the original XF through fluorination of the C=C bonds, whereas it decreased by chain-scission to form fluorocarbon gases such as CF_4. Chain-scission was accelerated to over 300 K in this study. The reaction temperature was set at room temperature for 72 h to fluorinate the C=C bonds without chain-scission.

Fig. 2 shows the relationship between weight change and reaction time at room temperature under 7 kPa F_2. The weight change of XF-H treated for 72 h was about 1.8 times greater than that of XF-F treated for 12 h. After 72 h, the weight increase was saturated. Consequently, the optimal condition for fluorinating C=C bond in XF without chain-scission was room temperature and 72 h here.

Fig. 3 shows FT-IR spectra of original PTFE, XF and fluorinated sample (XF-H). The peak due to the double bond ($-CF=CF_2$) (peak

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Table 1
Reaction conditions and decomposition temperatures for each sample treated by fluorination

Sample name	Reaction temperature (K)	Fluorine pressure (kPa)	Reaction time (h)	Decomposition temperature (K)[a]
XF	–	–	–	714
XF-A	R·T	51	24	725
XF-B	368	51	24	729
XF-C	373	51	24	730
XF-D	573	51	24	738
XF-E	593	51	24	740
XF-F	R·T	7	12	726
XF-G	R·T	7	24	728
XF-H	R·T	7	72	741
XF-I	R·T	7	168	731

[a] Measured from TG curves in Fig. 6; it was defined as the point at which the weight loss was 5%.

II) was detected at 1785 cm^{-1} in case of XF and XF-H [13–17,20]. There was the peak at 1794 cm^{-1} (peak I) which was identified as that for characteristic one of PTFE. There was one another peak (peak III) at 1820 cm^{-1} which might correspond to C=O as an impurity. Peaks I and III appeared in the spectra of PTFE, while peak II did not. So, peak II have to correspond to $-CF{=}CF_2$ bond in XF samples. The peak intensity ratio of peaks I and II, I_{PTFE}/I_{PTFE} is the convenient parameter which reflects the content of $-CF{=}CF_2$ bond in the sample. I_{PTFE}/I_{PTFE} values were 0.76 and 0.14 for XF and XF-H, respectively. The $-CF{=}CF_2$ bond in the sample seems to be converted into $-CF_2-CF_3$ bond by fluorination. Although this $-CF_2-CF_3$ bond must have the absorption at 1400–1000 cm^{-1}, the absorption of these samples at those wavenumbers was so strong that the reliable data cannot be obtained. From the results of I_{PTFE}/I_{PTFE} values, 20% of $-CF{=}CF_2$ bond still exists in the sample even after fluorination. This may be caused by that some $-CF{=}CF_2$ bond exists at the inside of the sample where F_2 gas cannot permeate to.

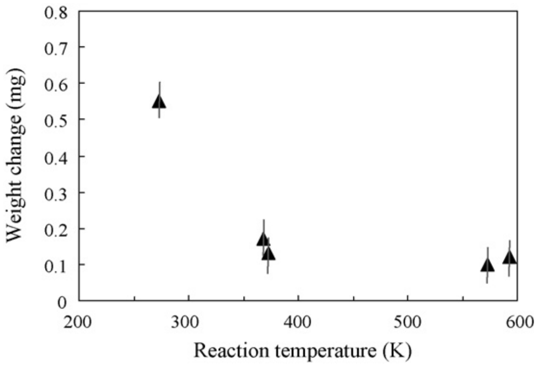

Fig. 1. Relationship between weight change and reaction temperature under 51 kPa F_2 for 24 h.

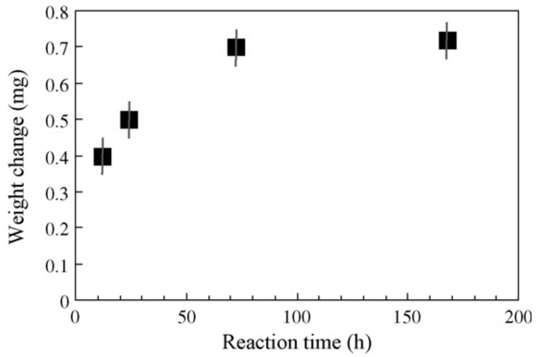

Fig. 2. Relationship between weight change and reaction time at room temperature and 7 kPa F_2.

Thermal stability can also be evaluated by using heat-of-crystallization (ΔH_c) values [3,18,19]. Larger ΔH_c values in samples imply better thermal stability. Fig. 4 shows the relationship between reaction temperature and heat of crystallization (ΔH_c) for samples (▲) treated at 51 kPa $F_2$for 24 h. The heat of crystallization [18,21–23] was determined from the exothermic peak area at crystallization temperature (T_c) in DSC profiles. The ΔH_c values for samples (▲) are scattered as shown in Fig. 4. As described above, chain-scission occurred over 300 K. Dotted lines show average

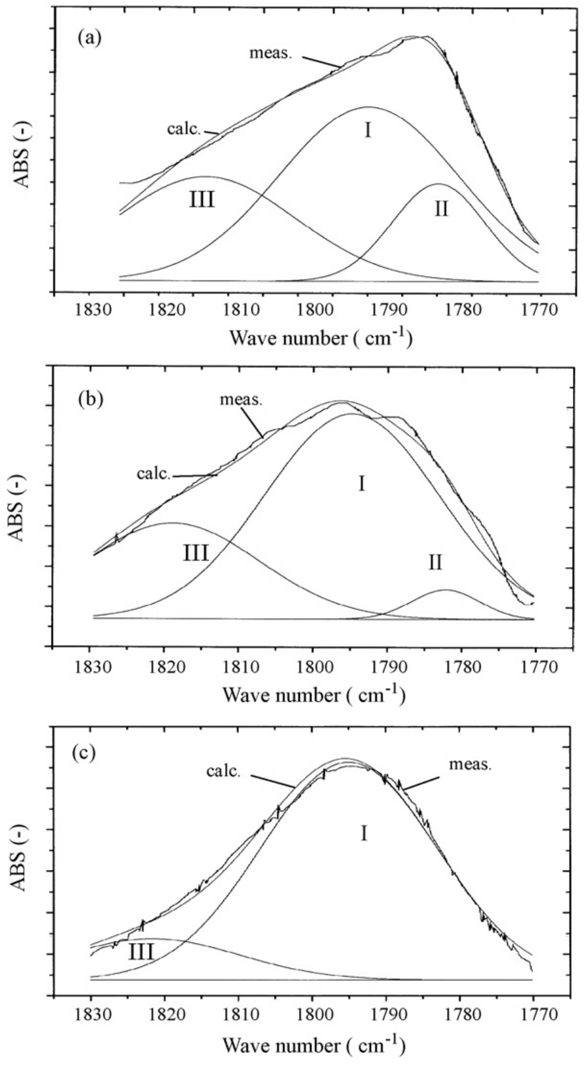

Fig. 3. FT-IR spectra around 1800 cm^{-1} with the results of peak the separation. (a) XF (original), (b) XF-H (fluorinated at room temperature for 72 h) and (c) PTFE.

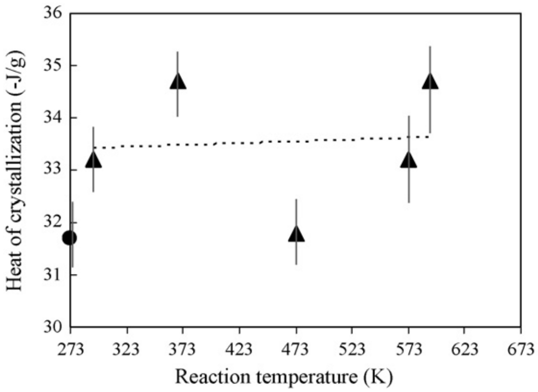

Fig. 4. Relationship between reaction temperature and enthalpy of crystallization (ΔH_c) in original XF, samples (▲) treated at 51 kPa for 24 h with F_2. [●: original XF; ▲: XF-A–XF-E].

values of ΔH_c. Average values of ΔH_c for fluorinated XF (▲) were about 2 J/g higher than that of original XF (●).

Fig. 5 shows the relationship between reaction times and heat of crystallization (ΔH_c) for samples (■) treated at room temperature and 7 kPa F_2. Compared with the change of ΔH_c values in Fig. 4, the ΔH_c values of samples fluorinated at room temperature increased gradually with increasing reaction time up to 72 h. It then decreased after 72 h. The ΔH_c values for fluorinated samples (■) were about 2 J/g higher than that of original XF (●), similar to that shown in Fig. 4. Therefore, the thermal stability of XF was improved through fluorination at room temperature in 72 h.

In addition, TG analysis was used to evaluate the decomposition temperatures of samples [14,19]. Decomposition temperatures for all fluorinated samples were estimated from TG curves shown in Fig. 6. Table 1 summarizes the results. Fig. 6 shows the weight as a function of temperature for various samples including PTFE as a reference, as measured using TGA analysis for 623–823 K with a heating rate of 2 K/min. The weight reached zero at 873 K for all samples including PTFE not shown in Fig. 6. The decomposition temperature of the sample (▲) treated at 51 kPa F_2 for 24 h increased monotonously, concomitant with the reaction temperature. Although fluorocarbon gases were released by the chain-scission, the thermal stability of XF was improved through fluorination at high temperature. The decomposition temperature of the sample (■) treated at room temperature and 7 kPa F_2 increased until 72 h and subsequently decreased. This result is consistent with those in Fig. 6(b). These results of DSC and TG analyses demonstrate that the thermal stability of XF can be improved through fluorination. But as shown in Fig. 3, $–CF{=}CF_2$ bond still exists in the sample after fluorination. That is the reason why the thermal stability of XF has been recovered to the same level as PTFE not completely by fluorination in this study.

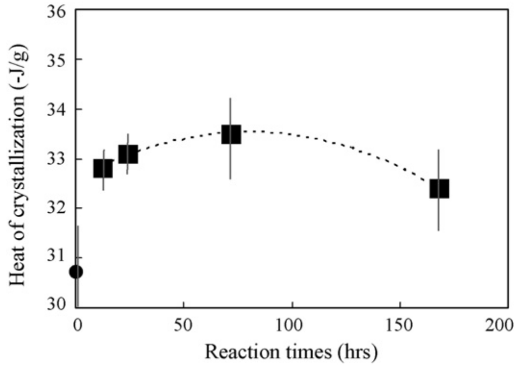

Fig. 5. Relationship between reaction times and enthalpy of crystallization (ΔH_c) in original XF, samples (■) treated at R·T and 7 kPa F_2. [●: original XF; ■: XF-F–H, J].

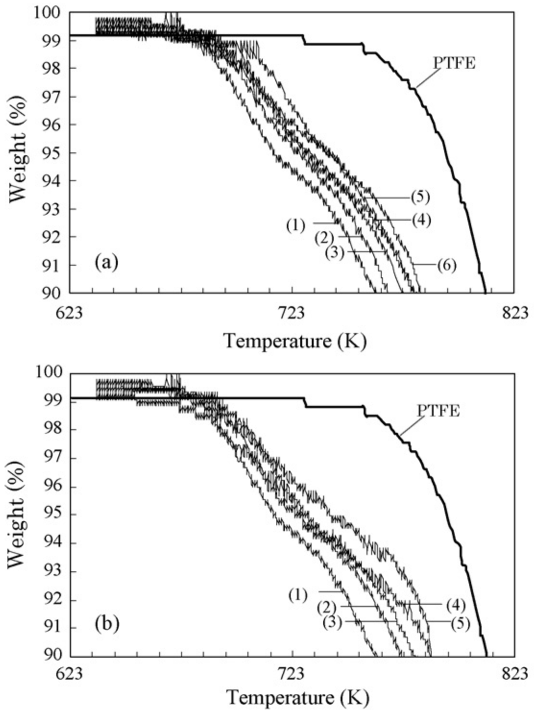

Fig. 6. Weight loss as a function of temperature for various samples by TGA analysis for 573–973 K with a heating rate of 2 K/min [(a): (1); XF, (2); XF-A, (3); XF-B, (4); XF-C, (5); XF-D, (6); XF-E, (b): (1); XF, (2); XF-F, (3); XF-G, (4); XF-J, (5); XF-H].

3. Conclusion

In order to approach the problem of poor thermal stability of crosslinked PTFE (i.e. XF), we attempted in this study to improve thermal stability by treatment with fluorine gas. Results of reactivity between XF and F_2 gas calculated from the weight change during fluorination show that XF fluorination was carried out at room temperature for 72 h. Weights of samples increased more than that of original XF by fluorinating the $C{=}C$ bonds, whereas they decreased by chain-scission to form fluorocarbon gases such as CF_4. The peak area of the double bond ($–CF{=}CF_2$) at 1785 cm^{-1} detected using FT-IR analysis was smaller than that of XF. Considering the peak intensity ratio, about 80% of the double bond in the sample was able to be fluorinated in this study. Average values of heat of crystallization (ΔH_c) for all fluorinated XF samples were about 2 J/g higher than that of original XF. The decomposition temperature calculated from TG curves increased monotonously with the reaction temperature at 51 kPa F_2 for 24 h. The decomposition temperature for the samples treated at room temperature and 7 kPa F_2 increased until 72 h and subsequently decreased. Consequently, the thermal stability of XF can be improved through fluorination. But the complete recover (the same level as PTFE) of the thermal stability cannot be achieved because of the residual double bond after fluorination.

4. Experimental

Crosslinked PTFE powder (Mn; 2×10^7, average diameter: 50 μm) used for experiments was acquired from Hitachi Electric Wire Co. Ltd. Fluorination for the crosslinked PTFE (i.e. XF) was carried out using a fluorine apparatus manufactured by ourselves;

a reactor was made of nickel. Samples (1.25 g) were fluorinated by using various reaction conditions. Reaction temperature, fluorine pressure and reaction time were set respectively at 293–593 K, under 0.7–101 kPa and for 1 h to 7 days. The reaction temperature was controlled below 600 K to protect a melting of XF. Thermal stability of fluorinated XF samples was investigated using results of decomposition temperature calculated from TG curves at temperatures of 573–873 K in airflow (12 $dm^3 h^{-1}$) using a TG/DTA apparatus (TG/DTA32; Seiko Instruments Inc.). The decomposition temperature was defined according to one reference as the point at which weight loss occurred to 5% [19]. The XF chemical structure was examined using FT-IR analysis (Thermo-Nicolet 380). Differential scanning calorimetry (DSC) showed the melting point and enthalpy of crystallization (ΔH_c).

References

[1] M. Tutiya, Jpn. J. Appl. Phys. 11 (1972) 1542–1546.
[2] A. Oshima, S. Ikeda, T. Seguchi, Y. Tabata, Radiat. Phys. Chem. 49 (1997) 279–285.
[3] A. Oshima, Y. Tabata, H. Kudoh, T. Seguchi, Radiat. Phys. Chem. 45 (1995) 269–273.
[4] A. Oshima, T. Seguchi, Y. Tabata, Polym. Int. 48 (1999) 996–1003.
[5] J. Sun, Y. Zhang, X. Zhong, X. Zhu, Radiat. Phys. Chem. 44 (1994) 655–659.
[6] T. Katoh, D. Yamaguchi, Y. Satoh, S. Ikeda, M. Washio, Y. Tabata, Appl. Surf. Sci. 186 (2002) 24–28.
[7] Y. Tabata, A. Oshima, K. Takashika, T. Seguchi, Radiat. Phys. Chem. 48 (1996) 563–568.
[8] E. Katoh, H. Sugisawa, A. Oshima, Y. Tabata, T. Seguchi, T. Yamazaki, Radiat. Phys. Chem. 54 (1999) 165–171.
[9] D.M. Pinkerton, B.T. Sach, Aust. J. Chem. 23 (1970) 1947–1961.
[10] A. Oshima, A. Udagawa, S. Tanaka, Radiat. Phys. Chem. 62 (2001) 77–81.
[11] A. Oshima, T. Seguchi, Y. Tabata, Radiat. Phys. Chem. 55 (1999) 61–71.
[12] U. Lappan, U. Geibler, K. Lunkwitz, J. Appl. Polym. Sci. 74 (1999) 1571.
[13] U. Lappan, U. Geibler, K. Lunkwitz, Radiat. Phys. Chem. 59 (2000) 317–322.
[14] A. Oshima, S. Ikeda, E. Katoh, Y. Tabata, Radiat. Phys. Chem. 62 (2001) 39–45.
[15] Y. Tabata, S. Ikeda, A. Oshima, Nucl. Instrum. Methods Phys. Res. B 185 (2001) 169–174.
[16] X. Zhong, L. Yi, W. Zhao, J. Sun, Y. Zhang, Polym. Degrad. Stab. 40 (1993) 97–100.
[17] U. Lappan, U. Geibler, L. Haubler, D. Jehnichen, G. Pompe, K. Lunkwitz, Nucl. Instrum. Methods Phys. Res. B 185 (2001) 178–183.
[18] A. Oshima, F. Mutou, T. Hyuga, S. Asano, S. Ichizuri, J. Li, T. Miura, M. Washio, Nucl. Instrum. Methods Phys. Res. B 236 (2005) 172–178.
[19] J. Chen, M. Asano, T. Yamaki, M. Yoshida, J. Mem. Sci. 256 (2005) 38–45.
[20] K. Lunkwitz, U. Lappan, D. Lehmann, Radiat. Phys. Chem. 57 (2000) 373–376.
[21] T. Suwa, M. Takehisa, S. Machi, J. Appl. Polym. Sci. 17 (1973) 3253–3257.
[22] T. Kanazawa, Y. Haruyama, K. Yotsumoto, Report of Japan Atomic Energy Research Institute, JAERI-M, 1992, pp. 62–70.
[23] H. Kusano, S. Ikeda, A. Oshima, Dielectric-Insulation Material Research Report, DEI-96, 1996, pp. 132–142.