

Grafting of Multifunctional Groups onto the Surface of High-Strength Polyethylene Fibers and the Interface of Their Composites

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ABSTRACT: High-strength polyethylene (HSPE) fibers were oxidated via chemical reactions in an acidic medium, and the carboxyl group was transferred into the acyl chloride and then reacted with pentaerythritol or diethylene triamine to graft the multifunctional group compounds onto the surface of the HSPE fibers. Subtractive Fourier transform infrared spectroscopy and the methylene blue absorbing method were used to study the functional groups on the surface of the modified fibers and their content. The results show that the polar functional groups, including $-\text{COOH}$, $-\text{OH}$, and $-\text{NH}_2$, were introduced onto the surface of the

HSPE fibers, and the polar groups improved the wettability. The interface shear stress (IFSS) of the composites that were made from modified fibers and epoxy was measured by means of the microdebond method. The results show that the IFSS was greatly increased by the grafting of pentaerythritol or diethylene triamine onto the HSPE fiber surface.

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Key words: composites; FTIR; grafting; polyethylene (PE); interface shear stress

INTRODUCTION

Structural composites with high strengths and low densities that are made from fibers such as aramid, carbon fibers, and high-strength polyethylene (HSPE) fibers are beginning to be used routinely in place of more conventional metals and metallic alloys.^{1–3} HSPE fibers, composite-reinforced fibers, are made of ultra-high-molecular-weight polyethylene with a gel spinning method.^{4–6} The fibers exhibit the highest specific strength in manufactured fibers and are an important candidate fiber. HSPE fibers have been extensively applied in sails, cables, sporting goods, fishing nets, bulletproof vests, and more. However, the fibers have poor adhesive performance because of a lack of polar and functional groups. Moreover, their low melting point ($\sim 150^\circ\text{C}$) and large creep are barriers to their application in composites. Polyethylene has extremely low surface energy and polarity; therefore, its surface must first be treated to increase surface energy and to endow the surface with polarity for the purpose of improving adhesion.

Several methods for the surface modification of HSPE fibers, including plasma deposition,^{7,8} corona discharge,⁹ and surface photograft polymeriza-

tion,^{10–12} have been proposed to improve the adhesive performance of the interface between the fibers and a matrix. However, the improvements achieved from these methods may not be sufficient. It has been reported that the interfacial strength between carbon fibers and a matrix of epoxy can be improved with electrochemical oxidation, and the improvement of Kevlar fibers (Dupont) has also been shown.^{13–15}

The purpose of this study was to examine the application of the chemical oxidation process on the surface grafting of HSPE fibers. HSPE fibers were chemically oxidized in an acidic mixture solution of $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, and then the carboxyl groups were transferred into acyl chloride and reacted with pentaerythritol or diethylenetriamine. As we know, oxidation will damage HSPE fibers and decrease the strength of fibers. Therefore, the degree of oxidation was carefully controlled. The chemical grafting process can introduce multifunctional groups on the surface of HSPE fibers from one carboxyl group, which would result in a more effective improvement of the interfacial adhesion in their composites.

EXPERIMENTAL

Materials

The HSPE fibers used in the experiment were kindly supplied by the Chemical Fiber Institute, Donghua

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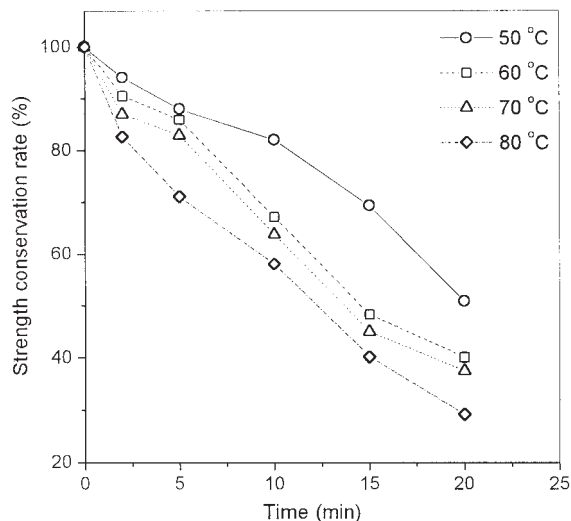


Figure 1 Changes in the tensile strengths of the HSPE fibers with chemical oxidation conditions.

University (Shanghai, China), which were manufactured by a gel spinning process with a denier-to-number filaments ratio of 1100:200 and a tensile strength of 20 CN/dtex. Epoxy resin (brand E51) and a room-temperature hardener (brand 593) were supplied by Shanghai Resin Factory (Shanghai, China). Potassium dichromate ($K_2Cr_2O_7$), concentrated sulfuric acid (H_2SO_4), acetone, and diethyl ether were used as received.

Surface modification of the HSPE fibers

Chemical oxidation of the HSPE fibers

The chemical oxidation treatment of HSPE fibers was performed as follows: the fibers were first dipped in a mixed solution (with a $K_2Cr_2O_7/H_2SO_4$ /distilled water ratio of 5:100:8) at 50, 60, 70, and 80°C. Then, the oxidized fibers were taken out and washed by distilled water and acetone two times. The oxidized HSPE fibers were thus obtained after the fibers were dried in an oven at 50°C for 24 h.

Grafting multifunctional group compounds onto the surface of HSPE fibers

The oxidized HSPE fibers (1 g) were reacted with an excess of $SOCl_2$ (15 mL) in benzene at 60°C for 20 min to transfer carboxyl groups into the acyl chloride, and then, they were washed by diethyl ether two times right after the completion of the chemical reaction to remove the excess $SOCl_2$. Then, the fibers with acyl chloride groups were placed into a solution of pentaerythritol (or diethylenetriamine) in *N,N*-dimethylformamide at 60°C for 2 h. The ob-

tained fibers were washed with distilled water and dried.

Measurements

The mechanical properties of the single fiber were tested on a tensile testing machine (YG001) (Changzhou Textile Machine Co., Ltd., China) with a special clamp.

The sedimentation rate was measured as follows: 100 single fibers 1 cm in length were placed in a mixed solution that consisted of isopropyl alcohol and water at a ratio of 1:7.7 to get a similar density solution of polyethylene. Some fibers floated on the surface of the mixed solution, and the others fell down to the bottom within 10 min. For convenience, the number of the latter was counted as the sedimentation rate.

The surface chemistry of the modified HSPE fibers was characterized with a Nicolet20SX-B Fourier transform infrared (FTIR) spectrometer. The content of functional groups on the surface of the fibers was measured by means of a methylene blue absorbing method described in the literature.¹⁶

The interface shear stress (IFSS) between the modified fibers and the matrix epoxy was measured with the microbond test method. A droplet of uncured resin, which consisted of epoxy resin (E51) and hardener (593), was placed onto a single fiber and was cured in this position for 48 h at room temperature. Once cured, the diameter and embedded length of the droplets were measured with an optical microscope. The specimens were placed in a tensile testing machine (YG001) so that one fiber end was gripped, and the resin droplet was placed between two knife edges. The fibers were pulled against the knife edges, and the load was recorded. IFSS (τ , MPa) was calculated as follows:

$$\tau = \frac{F}{\pi dl} \quad (1)$$

TABLE I
Sedimentation Rate (%) of the Surface-Treated HSPE Fibers

| | Temperature and time of chemical oxidation treatment | | |
|----------------------------------|--|----------------|----------------|
| | 60°C for 5 min | 70°C for 5 min | 80°C for 2 min |
| Chemically oxidized fibers | 55 | 58 | 68 |
| Grafting with pentaerythritol | 78 | 83 | 85 |
| Grafting with diethylenetriamine | 90 | 94 | 96 |

The sedimentation rate of the as-received HSPE fibers was 19%.

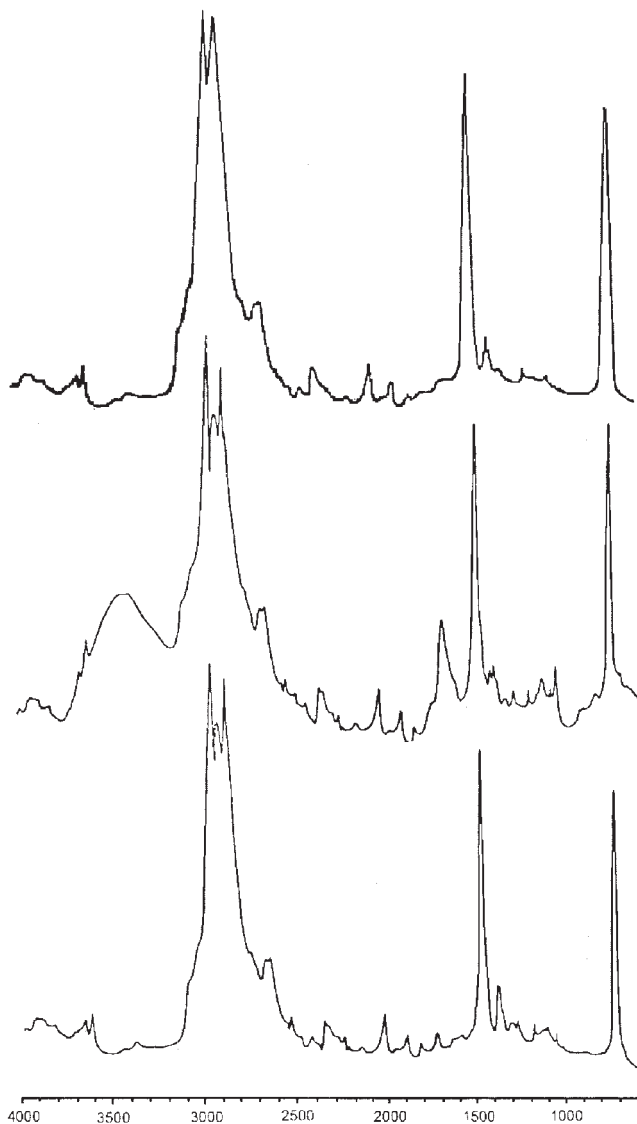


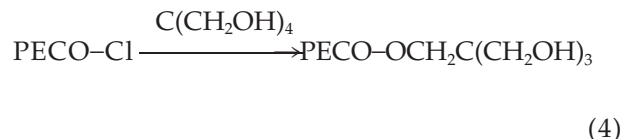
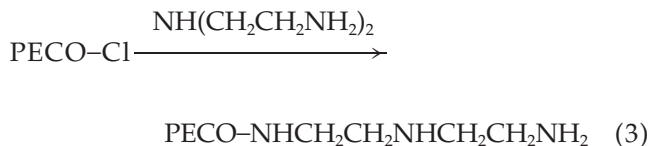
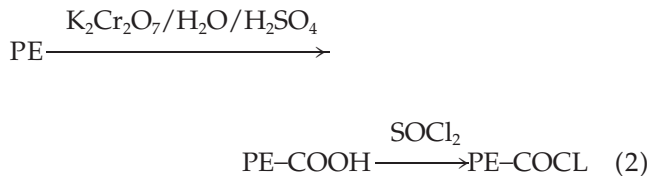
Figure 2 FTIR spectra of samples (a) PE1, (b) PE2, and (c) PE7.

where F (N) is the maximum load, d (mm) is the diameter of the fiber, and l (mm) is the embedded length. To reduce the data scatter, more than 20 specimens were prepared and measured.

RESULTS AND DISCUSSION

Chemical oxidation of HSPE fibers will decrease the tensile strength of the fibers, and this loss can be controlled by the adjustment of the degree of oxidation and the etched depth on the surface of the fibers. However, such controlling oxidation only produces fewer polar groups and limits the improvement in interfacial adhesion. To enhance the interfacial adhesion with as little damage to the fiber strength as possible, the following chemical reaction was designed to graft the multifunc-

tional group compounds onto the HSPE surface derived from one carboxyl group:



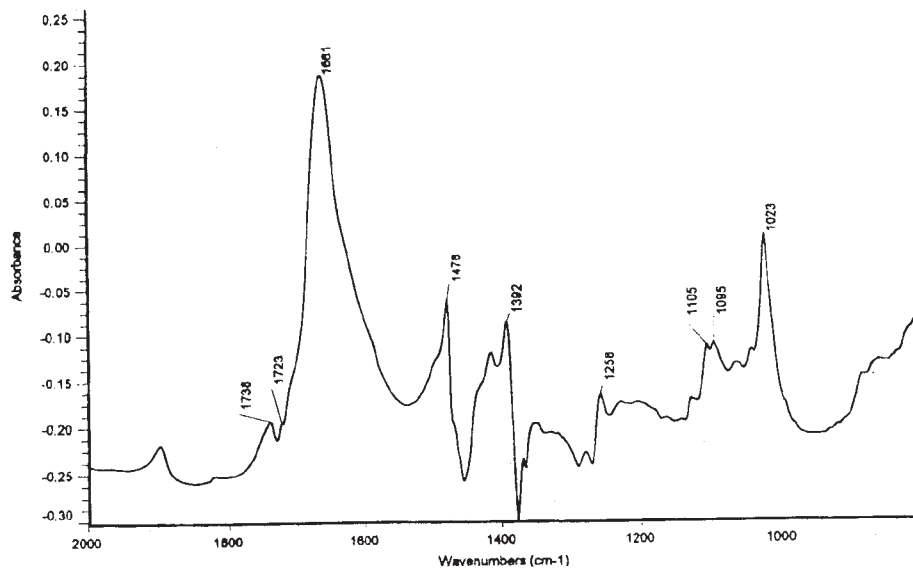
By this process, three to four active hydrogen groups were grafted onto the HSPE surface derived from one carboxyl group. These active hydrogen groups reacted with the epoxy resin to form the chemical bonding between the reinforcing fiber and the matrix resin, which benefited to the improvement of interface in the composite.

Figure 1 shows the effect of the chemical oxidation treatment on the strength of the HSPE fibers, which indicated that the strength of the treated HSPE fibers decreased with rising temperature and time for the chemical oxidation treatment system. For a strength conservation rate of more than 80%, the treated time needed to be less than 10 min at 50°C, 7 min at 60°C, 5 min at 70°C, and 2 min at 80°C.

As predicted, the surface modification with pentaerythritol or diethylenetriamine had no influence on the strength of the treated HSPE fibers. In other words, the modification only caused changes in the functional groups on the surface of the treated HSPE fibers.

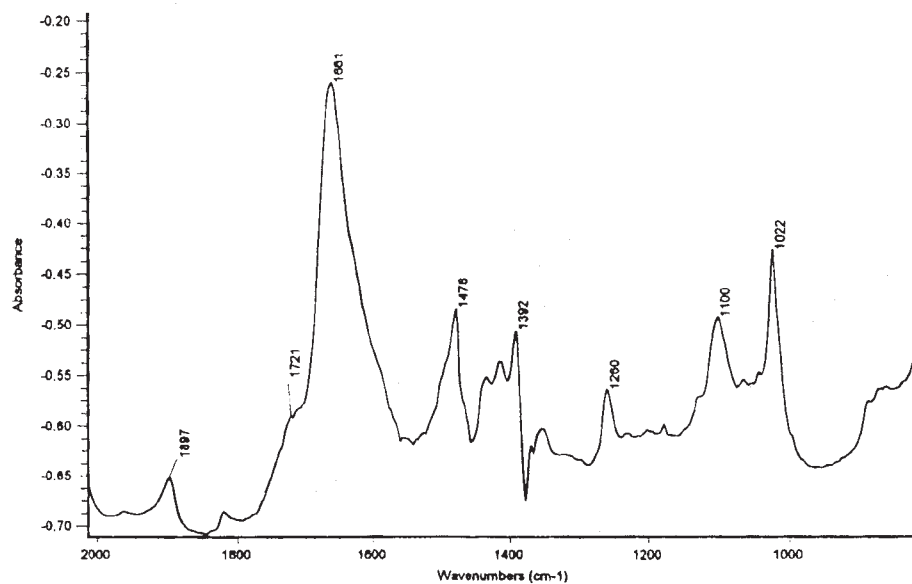
TABLE II
Codes of the HSPE Fiber Samples

| No. | Treatment method |
|------|---|
| PE1 | As-received fibers |
| PE2 | Oxidation at 50°C for 5 min |
| PE7 | Oxidation at 50°C for 5 min and then grafting with pentaerythritol |
| PE5 | Oxidation at 80°C for 2 min |
| PE10 | Oxidation at 80°C for 2 min and then grafting with pentaerythritol |
| PE11 | Oxidation at 80°C for 2 min and then grafting with diethylenetriamine |



SUBPE4 Subtraction GU031 PE7# - GU025 PE2#

(a)



SUBPE3 Subtraction GU031 PE7# - GU024 PE1#

(b)

Figure 3 Subtractive FTIR spectra of (a) PE7 - PE2 and (b) PE7 - PE1.

The wettability of the treated HSPE fibers was characterized via the measurement of the sedimentation rate of a sample in an aqueous solution. The higher the sedimentation rate of the sample was, the better the wettability was. An aqueous isopropyl alcohol solution with a density of 0.97 g/cm³ was used as the

measurement medium of the sedimentation rate. The sedimentation rates of the HSPE fibers are listed in Table I. The sedimentation rate of the as-received fibers (i.e., neither chemical oxidation treatment nor surface modification) was 19%, whereas that of the fibers treated by chemical oxidation or surface modi-

TABLE III
Content of Active Hydrogen Functional Groups on the Surface of the Treated HSPE Fibers

| Sample | Content of active hydrogen functional groups ($\mu\text{mol/g}$) |
|--------|--|
| PE1 | 0.227 |
| PE5 | 0.456 |
| PE10 | 3.16 |
| PE11 | 3.56 |

fication greatly increased. The higher the temperature of chemical oxidation was, the higher the sedimentation rate was. The wettability of the fibers was greatly improved when the chemically oxidized fibers were modified with pentaerythritol or even diethylenetriamine.

Figure 2 shows the FTIR spectra of the as-received and treated HSPE fibers whose treatment methods are listed in Table II. The shape of some peaks was similar for the low content of functional groups in the fibers; therefore, it was difficult to distinguish new peaks or intensities of the peaks. Subtractive spectra could overcome the difficulty, which is shown in Figure 3. The FTIR spectra of PE2 and PE7 [shown in Figs. 2(b) and 2(c)] and the subtractive FTIR spectrum of PE2 subtracted from PE7 [Fig. 3(a)] indicated an increase in hydroxyl groups and a decrease in carboxyl groups. The enhancement of the peaks at 3200–3640 and 1661 cm^{-1} indicated an increase in —OH groups, whereas a reduction in the peaks at 1738 and 1723 cm^{-1} indicated a decrease in —COOH groups. Stretching vibration peaks at 1023, 1105, and 1095 cm^{-1} were attributed to the single bond of C—O, which further indicated the reaction between pentaerythritol and the oxidized HSPE fibers. Another subtractive FTIR spectrum [Fig. 3(b)], PE1 subtracted from PE7, also indicated that —CO—, —CO—O—, and —C—O—H groups were introduced onto the surface of the HSPE fibers.

The content of active hydrogen functional groups on the surface of the fibers was measured by a methylene blue absorbing method. The results are listed in Table III, which shows that the content of functional groups for the oxidized fibers (PE5) increased by 100% and that for pentaerythritol and diethylenetriamine treatment increased greatly, compared with the as-received fibers.

To evaluate the effect of the oxidation and surface treatment for the HSPE fibers on the IFSS of the composites, a droplet of uncured epoxy resin was placed on the monofilament of the treated fibers and cured in this position. The IFSS of the samples was measured with the microdebond method. Figure 4 shows the plot of the microbound force versus the embedded length of the epoxy and PE10. The linear regression of the plot gave the IFSS, and the results are listed in Table IV. The IFSS of the composites with as-received

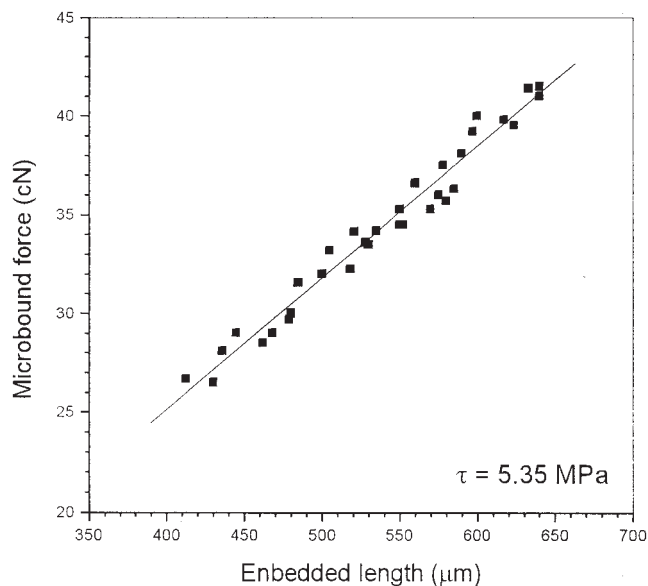


Figure 4 Microbound force versus the embedded length of the epoxy/PE10.

HSPE fibers as reinforced fibers was only about 1.45 MPa, whereas it increased up to 4.68 MPa for the oxidized fibers as reinforced fibers. The data listed in Table IV also shows that the IFSS improved when the temperature of the oxidation treatment was increased. Moreover, when pentaerythritol or diethylenetriamine was introduced on the surface of the oxidized HSPE fibers, the IFSS of the composites greatly increased. For example, when the HSPE fibers were treated by chemical oxidation at 80°C for 2 min and then transferred to diethylenetriamine groups, the IFSS of the composite increased up to 7.36 MPa, and the value was five times as that of the as-received fibers.

CONCLUSIONS

HSPE fibers were chemically oxidized in an acidic mixture solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 , and then, the carboxyl group was transferred to pentaerythritol or diethylenetriamine groups. The results from FTIR and

TABLE IV
IFSS (MPa) Between HSPE Fibers and Epoxy

| Treatment method of HSPE fibers | Temperature and time of oxidized treatment | | |
|----------------------------------|--|----------------|----------------|
| | 60°C for 5 min | 70°C for 5 min | 80°C for 2 min |
| Oxidation treatment only | 2.78 | 3.66 | 4.68 |
| Grafting with pentaerythritol | 3.83 | 4.44 | 5.35 |
| Grafting with diethylenetriamine | 6.04 | 6.59 | 7.36 |

The IFSS of the as-received HSPE fibers and epoxy was 1.45 MPa.

subtractive FTIR demonstrated that some polar functional groups, including —COOH and —OH, were introduced onto the surface of the HSPE fibers, which improved the wettability and interfacial adhesion of the fibers and matrices. Compared to the as-received HSPE fibers, the IFSS of the modified fibers with pentaerythritol or diethylenetriamine and epoxy increased by three to five times.

References

1. Kevorkjian, V. M. *Am Ceram Soc Bull* 1997, 76, 61.
2. Drzal, L. T.; Madhukar, M. *J Mater Sci* 1993, 28, 569.
3. Zhang, F. F. *Cailiao Gongcheng/J Mater Eng* 1994, 1, 8.
4. Cheng, J. L.; Fone, M.; Fu, Y. G.; Chen, W. *J Therm Anal* 1996, 47, 673.
5. Lee, D. M.; Chen, W. L.; Yen, M. T.; Chen, T. S. *Polym Eng Sci* 1995, 35, 1555.
6. Chodak, I. *Prog Polym Sci (Oxford)* 1998, 23, 1409.
7. Yang, J. M.; Huang, P. Y.; Yang, M. C.; Wang, W. *J Appl Polym Sci* 1997, 65, 365.
8. Ladizesky, N. H.; Ward, I. M. *J Mater Sci: Mater Med* 1995, 6, 497.
9. Lane, J. M.; Hourston, D. J. *Prog Org Coat* 1993, 21, 269.
10. Ranby, B.; Guo, F. Z. *Polym Adv Technol* 1994, 5, 829.
11. Ranby, B. *Polym Eng Sci* 1998, 38, 1229.
12. Amornsakchai, T.; Kubota, H. *J Appl Polym Sci* 1998, 70, 465.
13. Zhang, Z. Q.; Liu, Y. W.; Huang, Y. D.; Liu, L.; Bao, J. W. *Compos Sci Technol* 2002, 62, 331.
14. Shaker, M.; Kamel, I.; Ko, F.; Song, J. W. *Technol Res* 1996, 18, 249.
15. Gutowski, W. S.; Pankevicius, E. R.; Wu, D. Y. *Mater Sci Forum* 1995, 189–190, 211.
16. West, P. W.; Ramakrishna, T. V. *Anal Chem* 1968, 40, 966.