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Effect of Proton Irradiation on Mechanical Properties of Carbon/Epoxy Composites

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Irradiation using 120-keV protons was performed on the AG-80 epoxy resin and the unidirectional M40J/AG-80 composite. Changes in the bend strength, bend modulus, interlayer shear strength, and mass loss ratio were examined. Experimental results show that by using proton fluences lower than approximated, the cross-linking density increases with the fluence in the surface layer of the AG-80 epoxy matrix and increases the bend strength and modulus for the composite. Increasing the fluence above 6.3×10^{15} cm^{-2}, the cross-linking density, bend strength, and bend modulus are decreased. The mass loss ratios for both the AG-80 epoxy resin and the M40J/AG-80 composites increase with increasing proton fluence, and then level off.

Nomenclature

E' = storage modulus
T_g = glass temperatures
$\tan\delta$ = loss tangent

I. Introduction

CARBON/EPOXY composites are extensively used in structural components of spacecraft, such as in the truss structure, antennas, and solar-cell panels.[1] When spacecraft fly in orbit, components are exposed to a multitude of environments that are not present on the Earth, including high vacuum, plasmas, high-energy charged particles (protons and electrons), atomic oxygen, ultraviolet radiation, meteoroids and orbital debris, and thermocycling.[2–5] The interaction of these environments with spacecraft systems will cause degradation of materials. The damaging effects pose a difficult challenge for spacecraft designs. The aim of this study is focused on examining the radiation effect of protons with energy less than 200 keV on mechanical properties of carbon/epoxy composites.

Protons in the space environment have an extremely wide energy spectrum from 0 to more than 400 MeV. Fluxes of protons less than <200 keV protons are large.[6] Such protons can cause degradation of materials caused by a cumulative dose effect. Unfortunately, the need to perform applied research to understand their effect on mechanical properties of carbon/epoxy materials is often underestimated. To date, most previous work[7–10] was focused on the radiation effects in the energy ranges more than 1 MeV. Snead et al.[7] showed that the strengths of several thermoset epoxy resins and their composites were increased after proton irradiation. This increased strength was related to the curing agents, the amount of toughening agent, and the curing temperature of the resins. Zhang et al.[8] found that after 1.25-MeV proton irradiation, the bend strength and the compression strength of carbon/epoxy composites increased, while the tensile strength and the interlayer shear strength decreased. Romanov et al.[9] revealed that after the proton irradiation the surface color of epoxy resins became darker and changes in chemical and material properties depended on the irradiation dose. When the dose was less than 1.5–2.0 MGy, the curing process was dominant, being beneficial to formation of a three-dimentional net structure. The proton irradiation for the doses larger than 1.5–2.0 MGy destroyed the molecular chains of the epoxy resins severely, and the degradation dominated, leading to decreasing the tensile strength. The effect of >1-MeV proton irradiation on polymer films was characterized by DMA analysis.[10]

The need to design lighter and more complex spacecraft structures pushes the use of advanced carbon/epoxy composites. The AG-80 resin is a new type of thermosetting matrix for advanced polymeric composites, which can be stored for a long time at room temperature, and its glass temperature T_g is quite high (536 K) (Ref. 11). Also, the AG-80/DDS epoxy resin exhibits a unique resistance to moisture and heat.[12] It is necessary to examine its compatibility with space environments such as the proton radiation in order for its composites to be successfully used in spacecraft. In this paper, the changes in mechanical properties and mass loss of M40J/AG-80 composites were investigated after exposure to 120 keV protons and using dynamic mechanical thermal analysis (DMA). This study was funded by a program that aims to develop new composites with good resistance to space environments for spacecraft structures, and a lot of additional work needs to be done. More matrix resin and fiber types will be chosen, and effects of other space environment factors would be investigated, such as the electron radiation, the combined radiation of protons and electrons, and the vacuum thermocycling.

II. Experiment

A commercial grade of AG-80 resin, that is, tetraglycidyl diaminodiphenyl methane, was used as the matrix material, supplied by the Shanghai Institute of Synthetic Resins in China. The chemical structure is shown in Fig. 1. Its epoxy value is approximately 0.80, and the curing agent is diaminodiphenyl sulfone. The M40J carbon fibers were chosen as the reinforcement for the composites, which were supplied by TORAY Company in Japan. The prepreg tape for the M40J/AG-80 composite specimens was laid on a mold board and placed in an autoclave for curing. The curing cycles were as follows: heating to 130°C from room temperature with the heating rate 1.5–2.0°C/min, and holding for 40–60 min at 130°C under the pressure of 0.6–0.7 MPa; then heating to 180°C with the rate 1.5–2.0°C/min and holding for 120 min; and finally, cooling to room temperature in the autoclave. The volume fraction of M40J fibers in the manufactured composites was approximately 60%.

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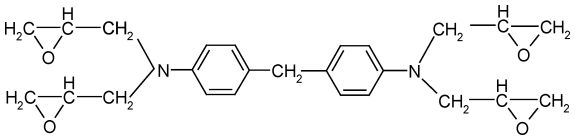

Fig. 1 Chemical structure of AG-80 resin.

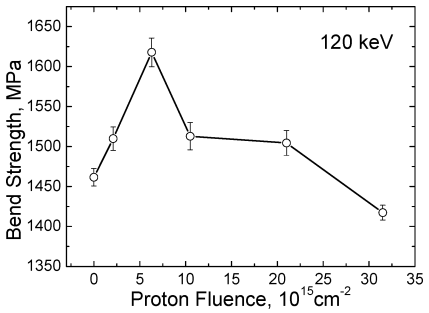

Fig. 2 Bend strength vs fluence for M40J/AG-80 composite irradiated with 120-keV protons.

The proton irradiation test was performed in a simulator with an energy range of 30–200 keV. Specimens were placed in the chamber with vacuum 1.2×10^{-5} Pa. The proton beam was perpendicular to the specimen surface. The energy of protons was chosen as 120 keV and the flux 6.25×10^{12} cm$^{-2} \cdot$ s^{-1}. The fluence was varied in the range of 2.1×10^{15}–3.15×10^{16} cm^{-2}. A liquid-nitrogen screen is inside the test chamber, keeping the environment temperature at 186 ± 3 K. According to TRIM program,[13] the penetration depth of 120-keV protons into the AG-80 epoxy resin is less than 2 μm.

The mass loss of precision after the irradiations was measured using a high-precision microbalance with a sensitivity of 10^{-5} g. The bend strength and interlayer shear strength were measured using a MTS-810 type tester. The sizes of specimens were $55 \times 12.5 \times 1.0$ mm for the bending and $30 \times 6.0 \times 4.0$ mm for the interlayer shearing. Each group of specimens consisted of five samples. The tests were performed by means of a standard three-point bending, and tensile stress was applied on the specimen surface layer irradiated by protons. The fractures of the specimens were observed by a HITACHI S-570 type scanning electron microscope. The DMA analysis was conducted using a Rheometric Scientific DMA V-type device, in which the deformation mode was a single-suspension type, the loading frequency 1 Hz, the temperature range from -110 to $+300$°C, and the heating rate 5°C/min. The DMA sample size was $22 \times 6.0 \times 0.8$ mm.

III. Results and Discussion

A. Bend Strength

Figure 2 shows the bend strength as a function of proton fluence for the M40J/AG-80 composite with increasing proton irradiation fluence. The bend strength increases then decreases after exposure to fluences higher than 6.3×10^{15} cm^{-2}. The trend change in bend modulus is similar to the trend in bend strength, as shown in Fig. 3.

Figure 4 shows the change in fracture surface morphology of the bending specimens after the proton irradiation for various fluences. In the figure, arrow A stands for the irradiated surface, arrow B for the epoxy resin matrix nearby the surface, arrow C for the carbon fibers, and arrow D for the epoxy matrix away from the surface. Before the irradiation, many small wrinkles appear on the epoxy matrix nearby the irradiated surface, which are almost parallel in distribution, as shown in Fig. 4a. This indicates that the pristine epoxy matrix has a given ductility. The fracture of the epoxy matrix in the vicinity of the irradiated surface exhibits an obvious curling feature after the irradiation for the fluence 6.3×10^{15} cm^{-2}, as shown by arrow B in Fig. 4b, demonstrating a fracture mode with better ductility. The fracture of the epoxy matrix away from the irradiated surface, as shown by arrow D, is similar to that for the pristine specimens. When the fluence increases to 3.15×10^{16} cm^{-2}, the

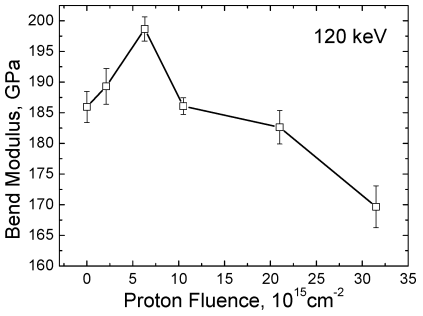

Fig. 3 Bend modulus vs fluence for M40J/AG-80 composite irradiated with 120-keV protons.

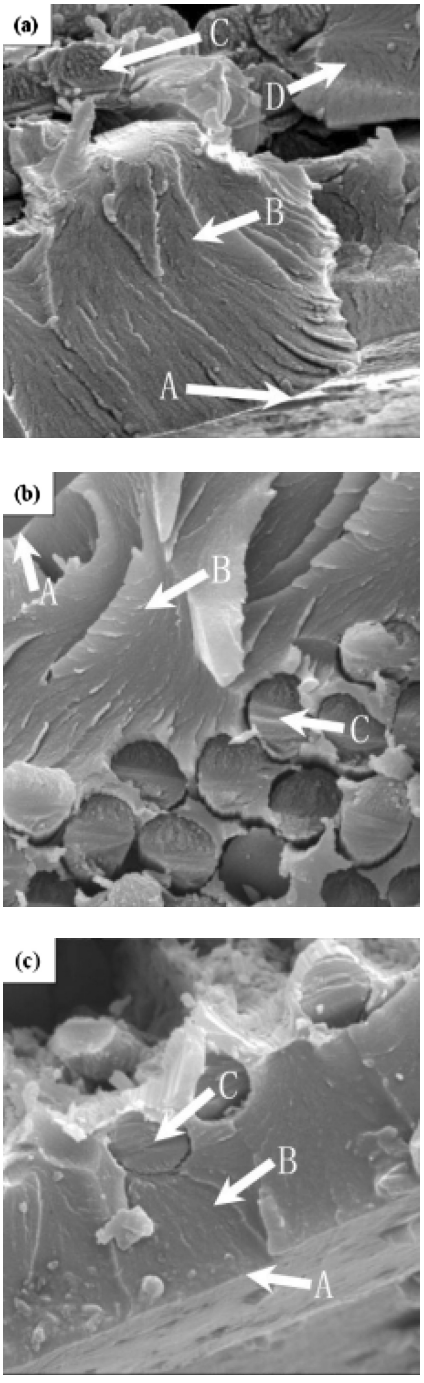

Fig. 4 SEM micrographs showing fractures of bend specimens irradiated with various fluences for M40J/AG-80 composite: a) before irradiation, b) 6.3×10^{15} cm^{-2}, and c) 3.15×10^{16} cm^{-2}.

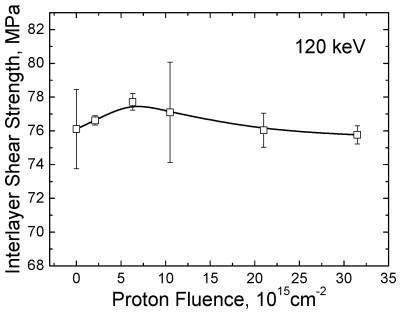

Fig. 5 Interlayer shear strength vs fluence for M40J/AG-80 composite irradiated with 120-keV protons.

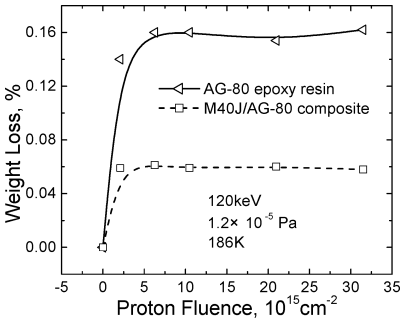

Fig. 6 Mass loss ratio vs fluence for AG-80 epoxy resin and M40J/AG-80 composite irradiated with 120-keV protons.

fracture of the epoxy matrix in the surface layer is rather smooth and has a typical brittle fracture feature (Fig. 4c).

B. Interlayer Shear Strength

Figure 5 shows the interlayer shear strength vs proton fluence. Increasing the fluence slightly increases the interlayer shear strength. This shear strength then decreases gradually after exposure to a fluence level of 6.3×10^{15} cm^{-2}. The change of the interlayer shear strength is similar in trend to the bend strength, but smaller in magnitude. The interlayer shear strength depends on both the shear strengths for the epoxy matrix and the interfaces of fibers with the matrix. Because only a shallow surface layer of epoxy matrix (approximately 2 μm in thickness) can be influenced by the 120-keV protons, the effect of proton irradiation on the interlayer shear strength is much smaller.

C. Mass Loss

Figure 6 show the mass loss ratio vs proton fluence for the AG-80 epoxy resin and M40J/AG-80 composite, respectively. With increasing fluence, the mass loss ratios are increased followed by tending to level off for both the AG-80 resin and the M40J/AG-80 composite. The maximum mass loss ratio of the AG-80 resin is almost four times as large as that for the M40J/AG-80 composite. The author believes that the mass loss originates from two events. One is volatilization of the absorbed water and the minor amount of residual organic species after curing in the materials under high vacuum. The other is the outgassing of the volatile molecules in the AG-80 epoxy matrix, produced by the proton irradiation.

D. DMA Analysis

DMA analysis is a useful means to reveal the microscopic relaxation movement of polymer molecules. All of the micromovements of the lateral groups, the end groups, and the impurities could be revealed in dynamic relaxation spectrum at low temperatures. It is well known that the α peaks in the loss tangent ($\tan\delta$) vs temperature curves are closely related to glass transition.[10] Figure 7 shows the effect of proton fluence on the $\tan\delta$ in the primary α-transition region for the pristine AG-80 epoxy resin. Table 1 gives the glass temperatures T_g and the $\tan\delta$ values at the α-transition peaks exposed to various proton fluences. In general, an increase

Table 1 Values of T_g and $\tan\delta$ at α transition peaks for AG-80 samples irradiated with 120-keV protons for various fluences

Fluences	T_g, °C	Loss tangent $\tan\delta$ at α transition peaks
Unirradiated	221.62	0.65899
2.1×10^{15} cm^{-2}	221.45	0.5334
6.3×10^{15} cm^{-2}	228.14	0.49719
3.15×10^{16} cm^{-2}	218.24	0.681

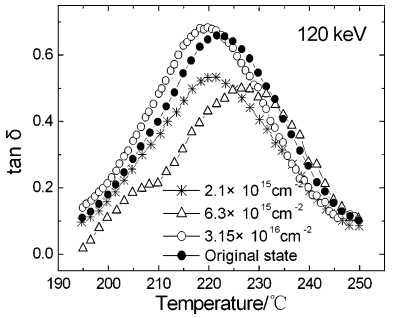

Fig. 7 DMA spectra of the primary α transition portion for AG-80 samples irradiated with 120-keV protons for various fluences.

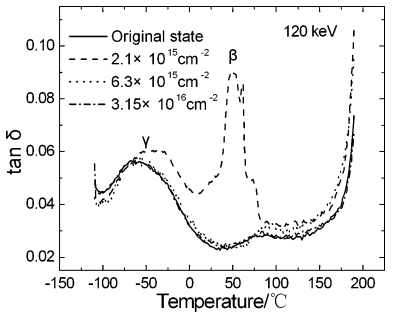

Fig. 8 DMA spectra of the secondary β and γ transition portions for AG-80 samples irradiated with 120-keV protons for various fluences.

of T_g and a decrease in the α-transition peak height can be related to the increase of cross-linking density in amorphous polymers. It was observed that using fluences lower than 6.3×10^{15} cm^{-2}, the T_g temperature increases and the peak $\tan\delta$ value decreases, indicating that the cross-linking density increases. Increasing the fluence above 6.3×10^{15} cm^{-2}, the T_g decreases and the peak $\tan\delta$ increases, indicating the cross-linking density decreases. Especially under the fluence 3.15×10^{16} cm^{-2}, the T_g temperature is even lower than that for the pristine sample. This phenomenon implies that under such a high fluence, the cross-linking density in the samples would be decreased quite severely.

Figure 8 shows the effects of proton irradiation on the two secondary transitions β and γ in the DMA spectrum for AG-80 epoxy resin. With increasing the fluence, the β transition peak intensity increases and reaches a maximum when exposed to proton fluences less than 6.3×10^{15} cm^{-2}. It was observed that the change in the β transition intensity with the fluence is similar to that for the cross-linking density and might be related to the excited movement of some specific groups in the molecule chains, such as the benzene rings. In contrast, the γ transition intensity does not change a lot after the proton irradiation. Usually, the γ transition occurs at the temperatures from -120 to 50°C in the DMA spectrum and is related to the excited movement of the chain segments $-CH_2CHOH(R)CH_2-$ (Ref. 14). Such a chain segment can be formed by opening an epoxy ring in the process of curing. The less change in the γ transition peaks with the fluence indicates that the proton irradiation has no obvious influence on the $-CH_2CHOH(R)CH_2-$ chain segments. The proton irradiation could not make the residual epoxy rings open for further curing in the AG-80 resin.

Figure 9 shows the storage modulus E' vs temperature curves for the AG-80 epoxy resin before and after the proton irradiation. The

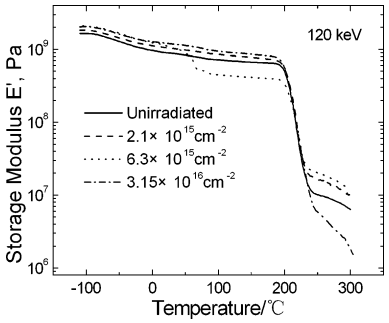

Fig. 9 DMA spectra showing storage modulus E' vs temperature for AG-80 samples irradiated with 120-keV protons for various fluences.

storage modulus is a parameter related to the elastic behavior of materials when undergoing small amounts of cyclic deformation. It is shown that under the fluence 6.3×10^{15} cm^{-2} the storage modulus E' dramatically drops at 60°C. In the elevated temperature range higher than T_g from 240 to 300°C, the E' increases with the fluence until 6.3×10^{15} cm^{-2} and is less than the value for the pristine samples using a fluence of 3.15×10^{16} cm^{-2} Also, the E' for the latter case drops severely with increasing the DMA testing temperature, demonstrating that the samples are melted. The increase in E' with proton fluence in the DMA testing temperature range higher than T_g could be attributed to increasing the cross-linking density and the melting of the samples at the temperatures higher than 240°C to degradation of the polymers.[10] It is believed that increasing the fluence until 6.3×10^{15} cm^{-2} results in increasing, cross-linking density. Increasing the fluence to 3.15×10^{16} cm^{-2} produces severe degradation in the AG-80 samples. This result is consistent with that obtained by the preceding primary α transition.

E. Discussion

The preceding results show that a change takes place for both the mechanical properties of the M40J/AG-80 composite, including the bend strength and modulus as well as the interlayer shear strength, and the cross-linking density in the AG-80 epoxy resin before and after the proton fluence of approximately 6.3×10^{15} cm^{-2}. Exposed to fluences lower than 6.3×10^{15} cm^{-2}, the mechanical properties and the cross-linking density increase with proton fluence. Further increasing the fluence results in a decrease of mechanical property and cross-linking density. It is suggested that the competition between debonding and bonding would play a major role in controlling the changes in cross-linking density and mechanical properties. In the early stages of proton irradiation, a small amount of debonding might take place at some chain segments with lower bonding energy, forming a portion of new free radicals. These free radicals could induce the possibility of cross linking for the neighboring chains in some regions with lower resistance to spatial positions. Increasing the proton fluence increases the amount of newly formed radicals and thus increases the cross-linking density. However, with further increasing the fluence the debonding would dominate, and the network structure of the AG-80 molecules could be destroyed severely. Also, with the network structure being destroyed, a variety of minor molecule products would be formed and vent out of the samples by outgassing. As a result, the cross-linking density must be reduced considerably. Therefore, the change in mechanical properties of the M40J/AG-80 composite is different before and after the proton fluence of approximately 6.3×10^{15} cm^{-2}.

IV. Conclusions

The 120-keV proton irradiation leads to nonmonotonous changes in mechanical properties of the M40J/AG-80 composite, including bend strength and modulus, as well as interlayer shear strength. Under the fluence lower than 6.3×10^{15} cm^{-2}, the bend strength and modulus increase with proton fluence. Continuing to increase the fluence tends to decrease these properties. The interlayer shear strength shows a similar trend.

DMA analysis shows that a change takes place at the proton fluence of approximately 6.3×10^{15} cm^{-2} for the change in cross-linking density in the AG-80 epoxy resin. Before the change, the cross-linking density increases with proton fluence. Continuing to increase the fluence tends to decrease the cross-linking density. The increase and decrease in the cross-linking density before and after the transit could account for the changes in the mechanical properties caused by the proton irradiation for the M40J/AG-80 composite.

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References

[1]Xiao, S. B., "Carbon Fiber and Carbon Fiber Composites Application on Satellites," *Hi-Tech Fiber and Application*, Vol. 24, No. 2, 1999, pp. 1–7.

[2]Zang, Z. Q., Gu, S. F., Shi, L. Q., and Wu, Z. H., "Study on Spacecraft Anomaly Caused by Space Environment," *Chinese Journal of Space Science*, Vol. 18, No. 4, 1998, pp. 342–347.

[3]Peng, G. R., Zhen, L., Yang, D. Z., and He, S. Y., "Effects of Vacuum Ultraviolet on Polymers," *Aerospace Materials and Technology*, Vol. 5, 2001, pp. 12–18.

[4]Wo, X. Y., Tan, F., and Chang, Y. D., "Effects of Space Environment on Polymer Composites," *Spacecraft Recovery and Remote Sensing*, Vol. 22, No. 4, 2001, pp. 58–60.

[5]Shin, K. B., Kim, C. G., Hong, C. S., and Lee, H. H., "Prediction of Failure Thermal Cycles in Graphite/Epoxy Composite Materials Under Simulated Low Earth Orbit Environments," *Composites Part B*, Vol. 31, 2000, pp. 223–235.

[6]Mikhailov, M. M., *Prediction of the Optical Properties of Thermal Control Coating Used in Spacecrafts*, Science Press, Novosibirsk, Russia, 1999, pp. 20–29.

[7]Snead, C. L., Jr., Morena, J., Czajkowski, C. J., and Skaritka, J., "Mechanical-Property Changes of Polymeric and Composite Materials After Low-Temperature Proton Irradiation," *Materials Characterization*, Vol. 42, 1999, pp. 73–91.

[8]Zhang, J. K., Ji, Y. F., and Li, Z. H., "Radiation Effects on Mechanical Properties of Carbon Fiber/Epoxy Composites," *Chinese Space Science and Technology*, Vol. 1, 1998, pp. 56–60.

[9]Romanov, V. A., Khorasanov, G. L., Konstantinov, I. O., Smolyanskii, A. S., Klinshpont, E. R., Tupikov, V. I., and Milinchuk, V. K., "Durability Changes of Epoxy Resins Under Action of Protons and Gamma Rays," *Radiation Physics and Chemistry*, Vol. 46, No. 4–6, 1995, pp. 863–866.

[10]Martínez-Pardo, M. E., Cardoso, J., Vázquez, H., and Aguilar, M., "Characterization of MeV Proton Irradiated PS and LDPE Thin Films," *Nuclear Instruments and Methods in Physics Research B*, Vol. 140, 1998, pp. 325–340.

[11]Gao, J. W., Shen, K., and Gao, Z. M., "The Cure Behavior of Tetraglycidyl Diaminodiphenyl Methane with Diaminodiphenyl Sulfone," *Thermochimica Acta*, Vol. 352–353, 2000, pp. 153–158.

[12]Wang, R., and Lan, L., "Development of Thermosetting Resin Matrix Used for Advanced Composite Materials," *Thermosetting Resin*, Vol. 16, No. 1, 2001 pp. 36–38.

[13]Ziegler, J. F., Biersack, J. P., and Littmark, U., *The Stopping and Range of Ions in Solids*, Vol. 1, Pergamon, New York, 1985, pp. 109–115.

[14]Luo, X. W., Ping, Z. H., Ding, J. P., Ding, Y. D., and Li, S. J., "Mechanism Studies on Water Sorption and Permeation in Epoxy Resin by Impedance Spectroscopy. II. Cure Kinetics of O-Cresol Novolac Resin with Esterfied Phenol Novolac Resin," *Journal of Macromolecular Science—Pure and Applied Chemistry*, Vol. A34, Nov. 1997, pp. 2279–2291.

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