

Emissivity of Chlorinated Polyethylene

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Synopsis

The emissivity of chlorinated polyethylene containing varying amounts of combined chlorine has been investigated. It was found that the emissivity of these compounds increases significantly with increase in chlorination.

INTRODUCTION

The study of the emissivity of polymers is important not only to define one of the thermophysical properties of polymers, but also to utilize the emissive properties of these materials in an effective way. Studies of the emissivity of polymers are not numerous compared to studies of infrared absorption spectra. Hence, a brief review of the major investigations is given below.

Emissivity values of chlorinated polyethylene can be varied at will through manipulation of the degree of chlorination and the appropriate polymer film thickness. Durana¹ and others²⁻⁵ studied the spectral emissivity of polymers to fully explore this thermophysical property. The broader aspects of total emissive behavior have been investigated by the authors.⁶⁻¹⁸ In the area of technical applications of polymers, investigations of surface temperature measurement by remote sensing,¹⁹ the use of polymers in solar energy collectors and greenhouses,²⁰ and the drying of polymers by radiation have received particular attention. The use of polymers in coating electronic printed-circuit boards and building materials has also been explored.^{21,22}

In experimental studies of the emissivity of polymers, special care must be exercised to define exactly the thickness and temperature of the material,^{4,14,19,22} the composition and structure of the polymer,^{2,5,8,9,12,15,16,18,20,25,27} and the substrate on which it is applied.^{1,8,22} To the extent that precision thermal radiation detecting instruments are not commercially available, each investigator must design a detector having the necessary attributes to perform the best observation under a given set of conditions.^{1,2,7,22} The following summarizes the points of the authors' previous studies.

First, a relatively simple apparatus for measurement of the emissive power from a polymer film was devised.⁷ Calibrations of the receiver were made by the specially prepared reference plate which was nearly equal to a blackbody, and the accuracy was checked by the samples with known emissivities.⁷

The emissivity of polymers depends chiefly on the composition and structure, combinations of different polymers,^{18,26} and the thickness of polymer film. The following expression includes these factors, especially in terms of $\epsilon_{p\lambda}$:

$$\epsilon_p(T) = \frac{1}{E_b(T)} \int_0^\infty \epsilon_{p\lambda}(T) E_{b\lambda}(T) d\lambda$$

where ϵ is emissivity, E is emissive power, T is temperature (about 300 K in this study), b is the blackbody (reference plate in this study), and λ is wavelength (almost infrared ray at about $T = 300$ K).

The polymer spectral emissivity is closely related to spectral absorptivity by Kirchoff's law.^{10,11} From Lambert's law, the spectral absorption is related to the absorption coefficient and thickness of the polymer film in the respective spectra.¹⁷

Polymer emissivities are affected much less by the degree of polymerization,^{12,14} latent heat of crystallization,¹⁴ temperature,²⁹ surface roughness in produced polymer films,^{13,28} and colors under the visible rays.^{8,29}

EXPERIMENTAL

Polymer Preparation

The series of chlorinated polyethylene samples used in the present study were obtained using conventional methods of polyethylene chlorination. Polyethylene chips (Sholex F131, $\rho = 0.922$) were chlorinated in carbon tetrachloride solution at 80°C using a constant flow of chlorine gas, the degree of chlorination being controlled by the length of the reaction period.²³ After a predetermined reaction period, the reacting mixture was purified three times by the reprecipitation method using a large volume of methanol and xylene. The chlorination process will not be discussed in detail in this report.

The comparatively thin films are obtained by pouring a 5% solution of chlorinated polyethylene in xylene over a glass plate in an atmosphere of a thermostatic box at 80°C and desiccating them carefully in a drying oven under reduced pressure at 40°C for 48 h.

Measurement of Emissive Power

The apparatus and method of measurement reported by the authors in earlier publications are outlined.^{7,8} Emissive power was measured by a thermopile made up of 52 sections of copper foils connected by Copper-Constantan wire and coated with a thin layer of soot. The receiver was set in a cylindrical copper enclosure and the temperature was kept at 0°C by ice water. Ice water was flowing through the interior route around the enclosure. Insulated cold junctions of the thermopile were attached to the bottom of the enclosure. Emissive power from a polymer film substrated on aluminum foil was detected by the thermopile when the shutter of the enclosure was opened. The zero balance of the thermopile was adjusted each time by closing the shutter.

Emissive power from the reference plate was measured by the same procedures. Emissivity of a polymer film can be compared to the emissive power of a reference plate under the same conditions. The measuring procedure in these studies consists in first detecting the emission from a chlorinated polyethylene with various amounts of combined chlorine and then comparing them with those of a reference plate ($\epsilon \approx 0.99$).⁷ All samples are deposited on an aluminum foil substrate and are measured at steady-state temperatures.

Figure 1 shows, respectively, examples of the emissive powers of the reference plate, aluminum foil, and a poly(ethylene terephthalate) film as a function of

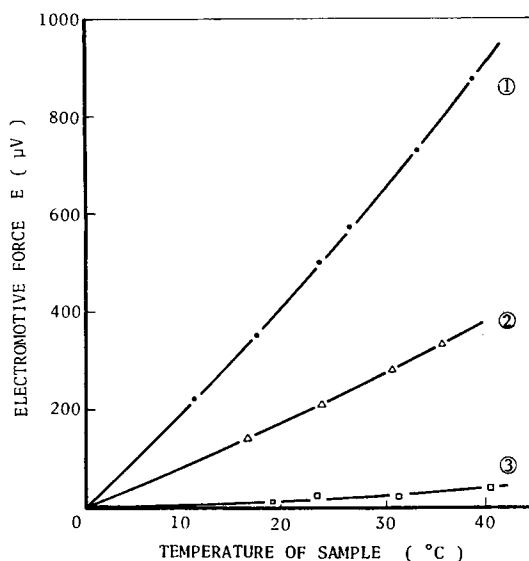


Fig. 1. Emissive power of several materials as a function of temperature: ① reference plate ($\epsilon \approx 0.99$); ② poly(ethylene terephthalate) (9- μ m thick film); ③ aluminum foil.

temperature. As demonstrated by previous studies^{7,8} and these results, this apparatus and method of measurement can be regarded as appropriate for measuring polymer emissivity. Figure 2 shows the emissive power of chlorinated polyethylene with various amounts of combined chlorine as a function of temperature. The emissive powers of the original unchlorinated polyethylene films and poly(vinyl chloride) films are shown in Figures 3 and 4. The latter were measured for the purpose of comparing the results with those of the chlorinated polyethylenes.

RESULTS AND DISCUSSION

The emissivities of chlorinated polyethylene are obtained by taking the ratios of the observed emissive power of the materials to that of the reference plate at the same temperature. Thus, Figure 5 presents the values of the average emissivities as a function of degree of chlorination and film thickness. The emissivity at zero thickness represents the value of the bare aluminum foil substrate. Emissivities of the chlorinated polyethylene films increase with thickness and the addition of chlorine to the polyethylene molecules. The effect of chlorination is strong for initial degrees of chlorination.

Figure 6 shows the emissivity of chlorinated polyethylene as a function of chlorine content for various film thicknesses. The triangular points in this figure represent the values for poly(vinyl chloride) with 56% chlorine content.

Figure 7 shows that for thin films of polyethylene the addition of chlorine produces a linear change in the percentage increase of emissivity over a wide range of chlorination. On the other hand, for thicker films, the linearity is limited to small percentages of initial chlorination.

One further observes that for the same chlorine content, chlorinated polyethylene has larger emissivities compared to those of poly(vinyl chloride). This

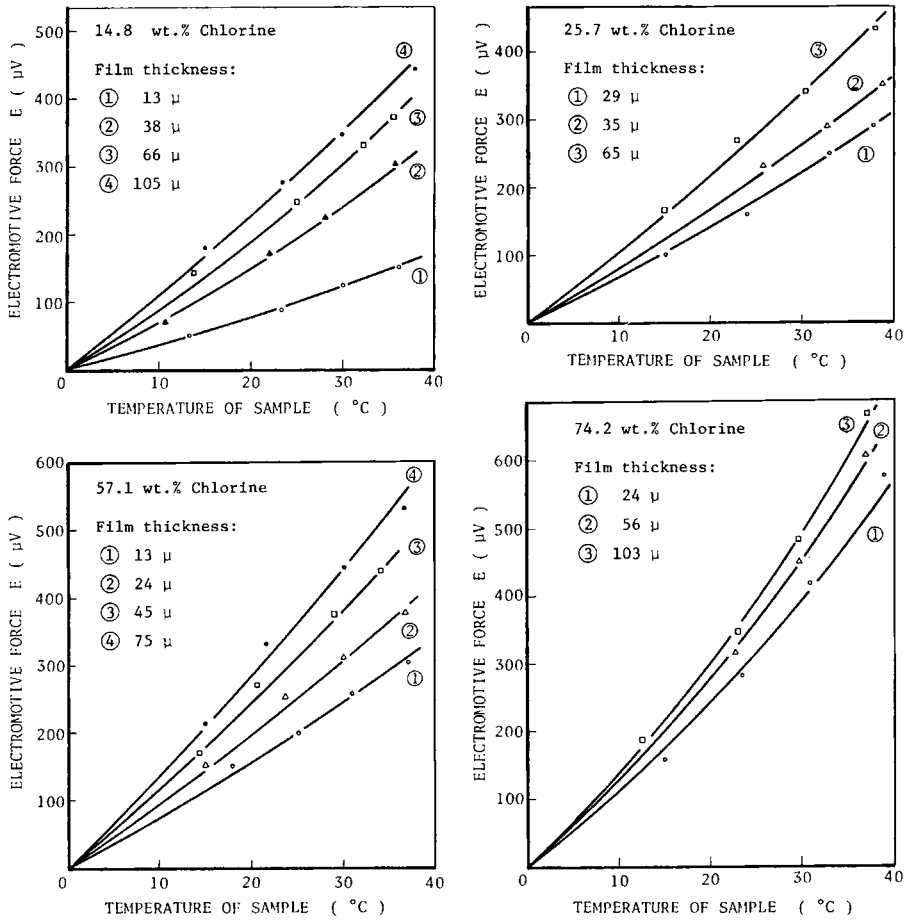


Fig. 2. Emissive power of chlorinated polyethylene films with varying chlorine concentrations, as function of temperature and thickness.

is explained by the following process. When polyethylene is chlorinated in carbon tetrachloride solution at 80°C using chlorine gas, chains of the type $-\text{CH}_2-\text{CH}_2-\text{CHCl}-$ and $-\text{CHCl}-\text{CH}_2-\text{CHCl}-$ will gradually appear until

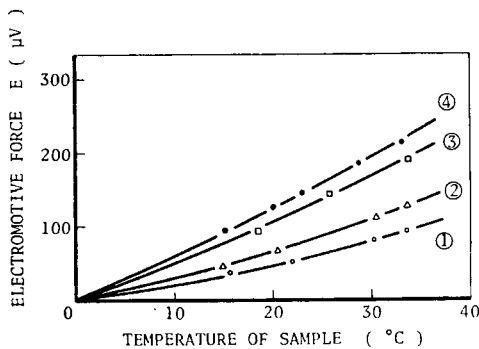


Fig. 3. Emissive power of polyethylene films. Film thickness: ① 19 μm ; ② 33 μm ; ③ 63 μm ; ④ 90 μm .

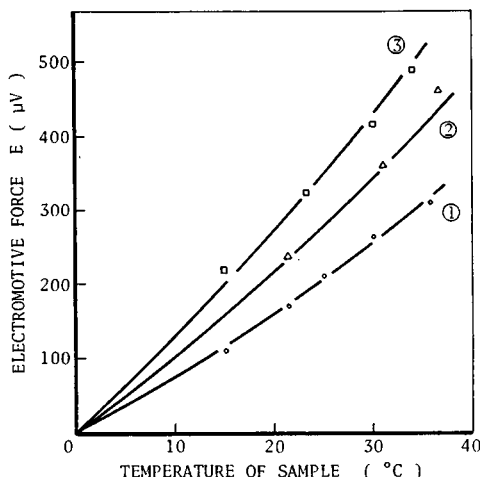


Fig. 4. Emissive power of poly(vinyl chloride) films. Film thickness: ① 16 µm; ② 38 µm; ③ 74 µm.

finally a structure such as —CHCl—CHCl—CHCl— is obtained.^{23,24} These chains of chlorinated polyethylene will be expected to absorb more of the infrared radiation over a large number of bands than poly(vinyl chloride). This causes the emissivities of chlorinated polyethylene to be larger than those of poly(vinyl chloride).

Figure 8 shows, respectively, spectral distributions of the absorptive (emissive) power of a blackbody and the absorptive power of chlorinated polyethylene film and unchlorinated polyethylene film. The blackbody emissive power is calculated from Plank's spectral distribution law of emissive power at 300 K. In the

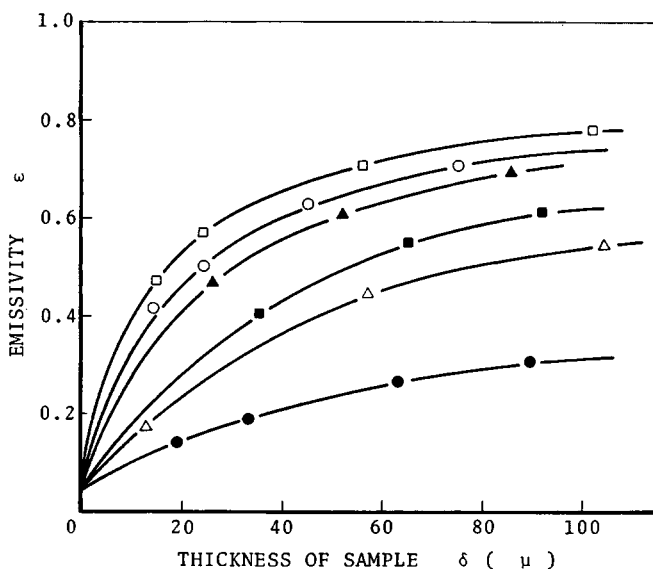


Fig. 5. Emissivity of chlorinated polyethylene films as function of thickness and chlorination. Degree of chlorination, in wt %: (●) 0 (polyethylene); (Δ) 14.8; (■) 25.7; (▲) 56.0 [poly(vinyl chloride)]; (○) 57.1; (□) 74.2.

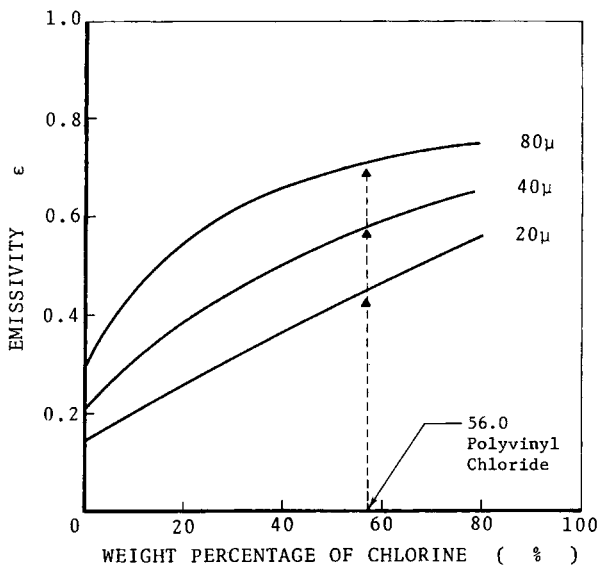


Fig. 6. Emissivity of chlorinated polyethylene films for various constant thicknesses, as function of degree of chlorination.

case of the polymers, their respective absorptive powers are obtained from the product of the blackbody spectral emissive power and their infrared spectral absorptive ratio.

It is recognized from this figure that chlorinated polyethylene absorbed more energy than unchlorinated polyethylene, notwithstanding the fact that the thickness of chlorinated polyethylene film was less than that of the plain polyethylene film. The increased absorptive power of the chlorinated polyethylene

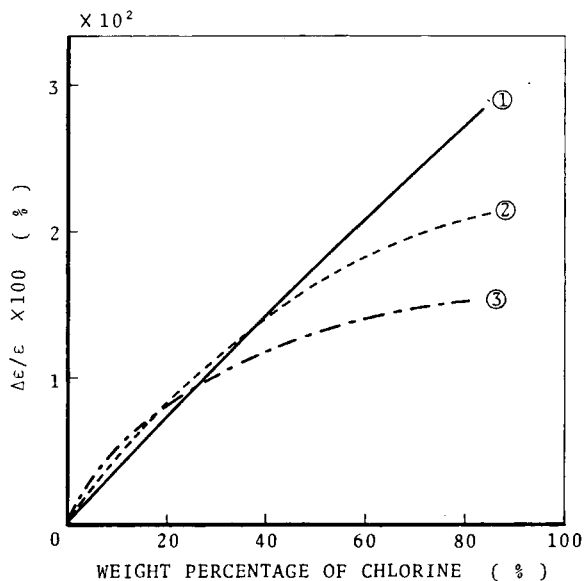


Fig. 7. Percentage increase in emissivity as function of chlorination for constant values of film thicknesses. Film thickness: ① 20 μ m; ② 40 μ m; ③ 80 μ m.

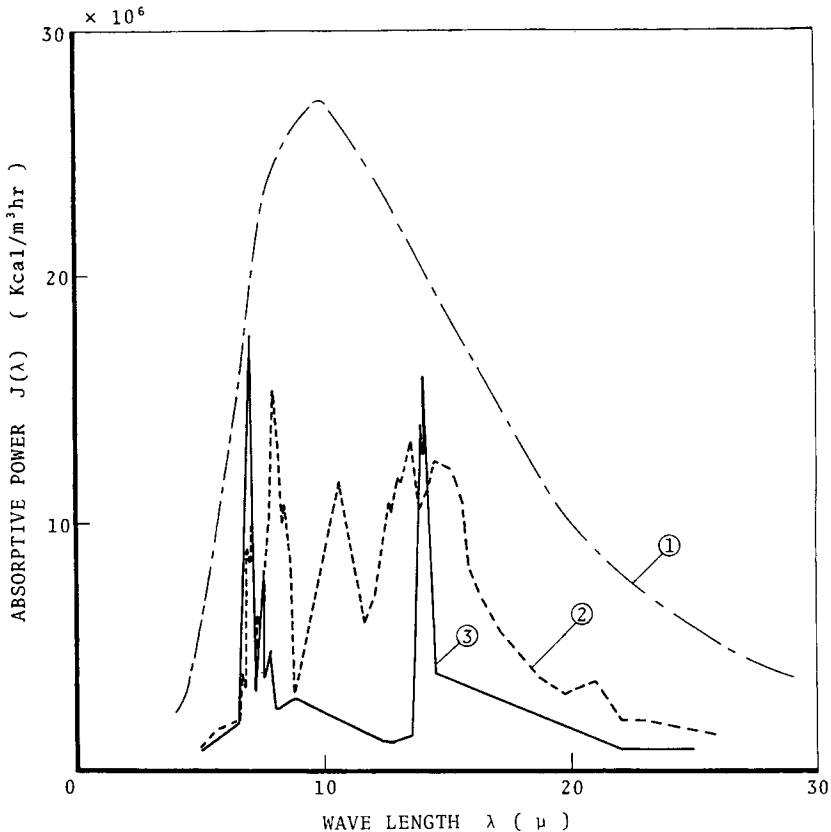


Fig. 8. Spectral distribution of absorptive power at 300 K: ① blackbody; ② chlorinated polyethylene film (16 μm thick, 73 wt % chlorine); ③ polyethylene film (23 μm thick).

is caused mainly by CCl stretching modes in the region 13–15 μm , CC skeletal modes in the region 9–11 μm , and CH deformation modes around 8 μm .²³ It is, therefore, quite natural that chlorinated polyethylene film radiates more than polyethylene film by reason of its increased absorption upon chlorination. This effect is illustrated by Figure 9. As a result, an increase in weight of polyethylene from 0.20 g to 0.72 g (when chlorinated to 74%) is accompanied by an increase in emissivity of nearly 300%.

CONCLUSIONS

A wide range of emissivities can be obtained through the chlorination of polyethylene films and by control of film thickness. These increased emissivities are probably caused by increased absorptivities causing CCl stretching, CC skeletal, and CH deformation modes.

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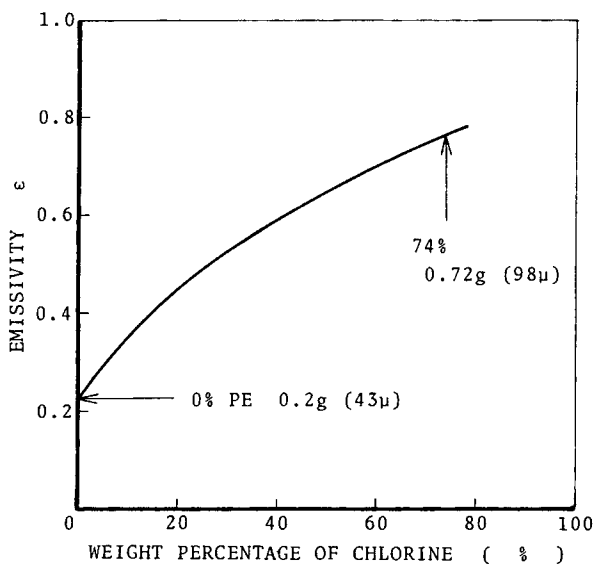


Fig. 9. Increase in emissivity as function of chlorination.

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