Emissivity Values for Poly(vinyl Chloride) with Varying Plasticizer Compositions

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Synopsis

The emissivity of plasticized poly(vinyl chloride) (PVC) containing varying compositions and amounts of plasticizer was investigated. The four plasticizers examined were dibutyl phthalate (DBP), dioctyl phthalate (DOP), diisodecyl phthalate (DIDP) (phthalic acid type), and dioctyl adipate (DOA) (adipic acid type). The emissivity of plasticized PVC film increased almost equally with the difference in the compositions between DOP and DOA. It was also clear that the emissivity of the plasticized PVC film decreased gradually with the molecular sequence length of DBP, DOP, and DIDP.

INTRODUCTION

It is generally recognized that pure PVC is limited in use due to its stiffness because of the strong intermolecular force originating from the chlorine. When the plasticizer is added to PVC, the modulus of elasticity and the glass transition temperature are reduced. Plasticized PVC has become widely accepted in manufacturing and industrial uses because of its improved elasticity and processing ability. For these reasons, such properties as the modulus of elasticity, glass transition temperature, and other properties of plasticized PVC have been fully studied. Plasticized PVC is a polymer that has wide commercial applications where emissive properties must be utilized effectively, yet few researchers (except for the authors) have measured its emissivity values.[1–6]

In this study, four different plasticizers were added to PVC. The emissivity values of these compounds were then determined for various amounts of these plasticizers. Investigations were made to explore the change of emissivity caused by the molecular structure and the sequence length of the plasticizers. The amounts of plasticizers used in this experiment were similar to the quantities of plasticizers commonly used in the commercial production of PVC.

EXPERIMENTAL

Cast Film Preparation

The series of plasticized PVC films used for this study was obtained by the casting method. One of the plasticizers was mixed thoroughly by stirring with a solution of PVC in tetrahydrofuran (5–10% concentration). Comparatively thin films were obtained by pouring these mixed solutions of predetermined concentrations over a level glass plate and then desiccating the films slowly in a well-ventilated room for more than 24 h at room temperature. Several other

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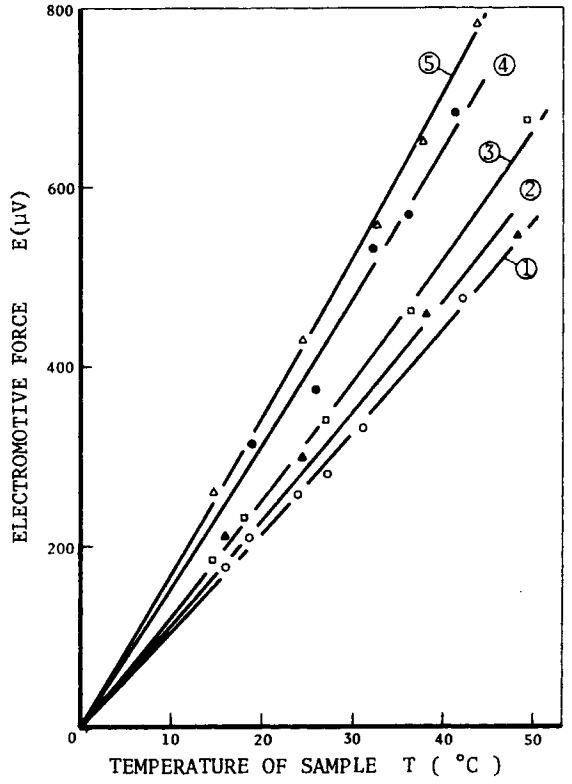


Fig. 1. Emissive power of poly(vinyl chloride) films: PVC film thickness: ① 23 μ; ② 29 μ; ③ 44 μ; ④ 112 μ; ⑤ 125 μ.

plasticized PVC films were produced for these experiments by use of the same procedures. The structural formulas for these four plasticizers are shown in Table I.

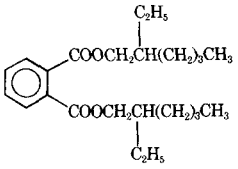
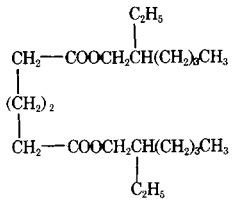
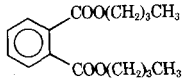
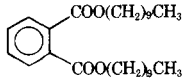
Measurement of Emissive Power

Procedures for making measurements were reported by the authors earlier.[7,8] First, the emission from a plasticized PVC film was detected on an aluminum foil substrate and then compared with a known reference plate ($\epsilon \simeq 0.99$).[7] Figure 1 shows the emissive power of the original unplasticized PVC films as a function of temperature and film thickness. Figure 2 shows the emissive powers of the plasticized PVC films with various amounts of DOP as a function of temperature. Emissive powers obtained for the other plasticizers—DOA, DBP, and DIDP—are shown in the same figures.

RESULTS AND DISCUSSION

The emissivities of the plasticized PVC films were obtained by taking the ratio of the observed emissive powers for the materials to those for the reference plate at the same temperature.[7,8] Thus, Figure 3 represents the values of the average emissivities for plasticized PVC films as a function of DOP content and film

TABLE I
Structural Formulas for Plasticizers

Symbol	Structural formula
DOP	
DOA	
DBP	
DIDP	

thickness. The emissivity at zero thickness represents the value of the bare aluminum foil substrate. Figure 4 shows the emissivities for PVC film plasticized by DOA. The emissivities obtained for DOA were similar to the values observed for DOP. Emissivities of the plasticized PVC films increased with the addition of DOP or DOA to PVC. The two plasticizers have nearly identical effects on emissivity at various film thicknesses.

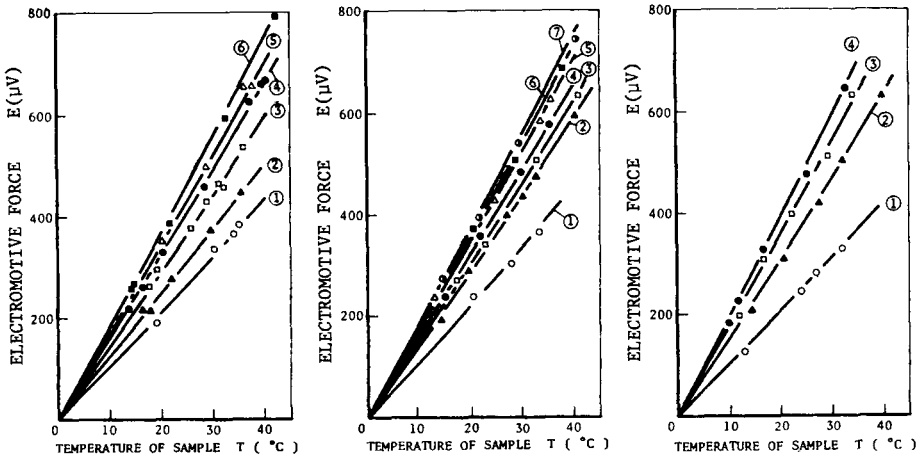


Fig. 2. Emissive power of plasticized PVC films, with various amounts of DOP, as function of temperature and thickness. (a) DOP 10%, film thickness: ① 20 μ; ② 30 μ; ③ 56 μ; ④ 78 μ; ⑤ 95 μ; ⑥ 120 μ. (b) DOP 25% film thickness: ① 17 μ; ② 45 μ; ③ 62 μ; ④ 96 μ; ⑤ 106 μ; ⑥ 121 μ; ⑦ 134 μ. (c) DOP 50%, film thickness: ① 15 μ; ② 54 μ; ③ 84 μ; ④ 177 μ.

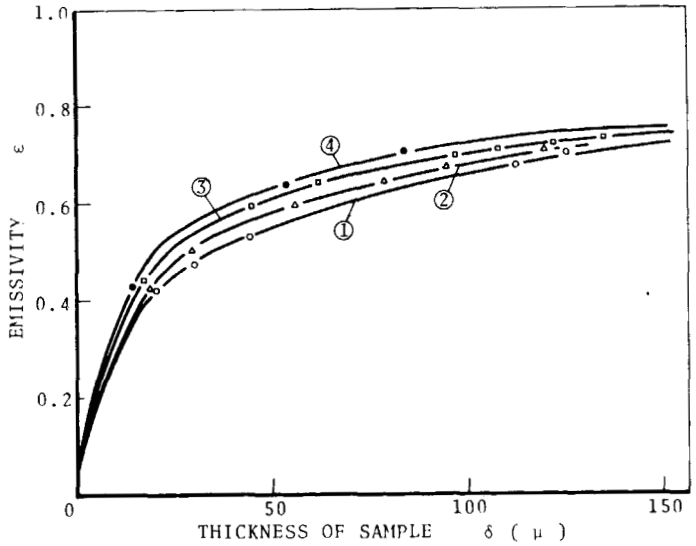


Fig. 3. Emissivity of plasticized PVC films as function of thickness and DOP content. DOP content, in wt %: ① 0 (PVC); ② 10; ③ 25; ④ 50.

Figure 5 shows the rate of increased emissivity as a function of film thickness for DOP and DOA. Also, the emissivity increases with the addition of more plasticizer. The curve has a maximum peak for a thickness between 15 and 30 μ. This thickness is widely used for solar energy collectors, greenhouses, and other applications. Also, it was observed that the position for the peak of the curve shifts slightly from a thick (30 μ) to a thin (15 μ) film thickness with addition of more plasticizer.

Figure 6 shows the rate of increased emissivity as a function of DOP and DOA content for the various constant film thicknesses. For example, a plasticized

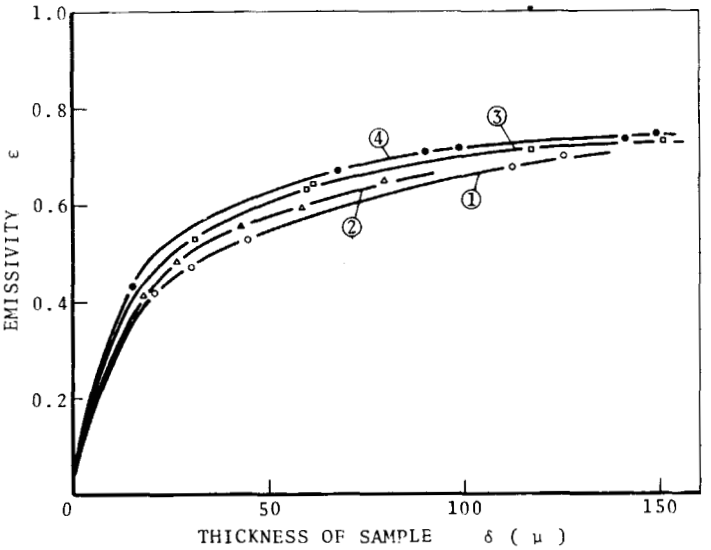


Fig. 4. Emissivity of plasticized PVC films as function of thickness and DOA content. DOA content, in wt %: ① 0 (PVC); ② 10; ③ 25; ④ 50.

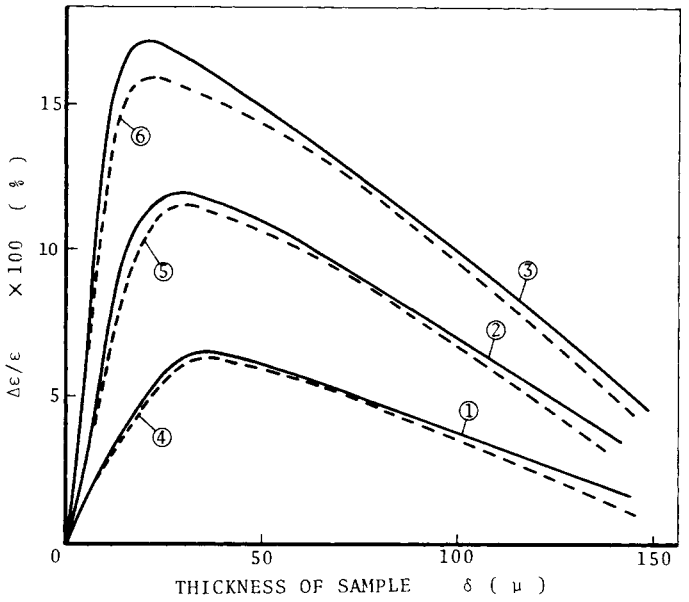


Fig. 5. Rate of increased emissivity as function of film thickness for DOP and DOA constant contents. Plasticizer content, in wt %: DOP: ① 10; ② 25; ③ 50. DOA: ④ 10; ⑤ 25; ⑥ 50.

PVC film 20 μ thick showed an increase of approximately 15% in emissivity when the plasticizer content was 45%.

The increase in emissive power for PVC which was caused by addition of the plasticizer shows improved infrared absorptive spectra for the polymers because a good emitter is also a good absorber.

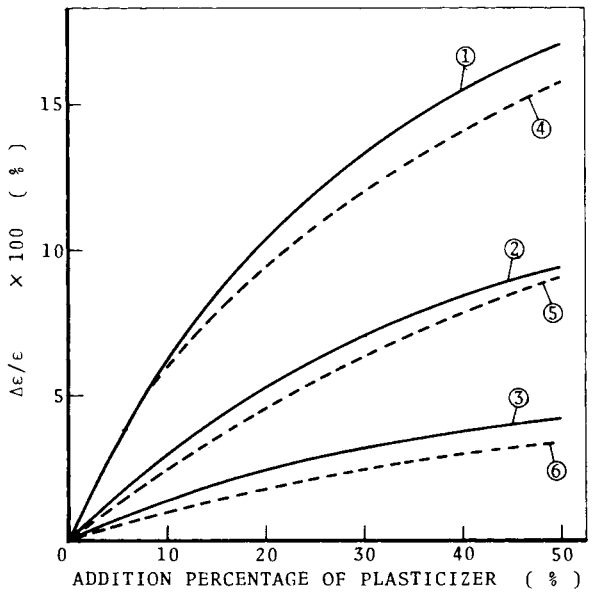


Fig. 6. Rate of increased emissivity as function of DOP and DOA content for constant film thickness. Film thickness: DOP: ① 20 μ; ② 100 μ; ③ 150 μ. DOA: ④ 20 μ; ⑤ 100 μ; ⑥ 150 μ.

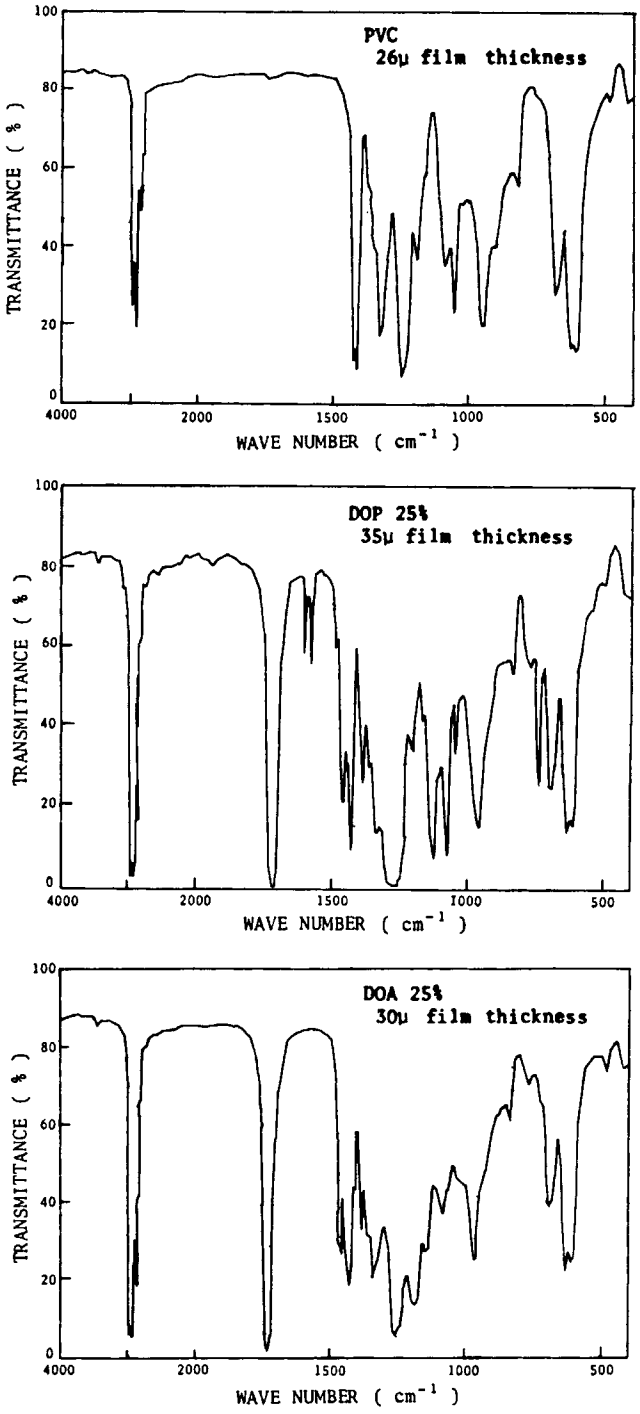


Fig. 7. Infrared spectra of PVC and plasticized PVC films with plasticizer content of 25%.

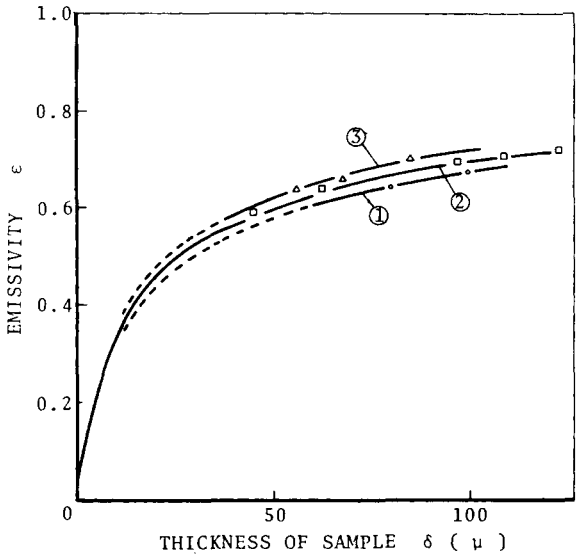


Fig. 8. Emissivity of plasticized PVC films as function of thickness for three different plasticizers with content of 25%. Plasticizer: ① DIDP; ② DOP; ③ DBP.

Figure 7 shows that the infrared absorptive spectra for PVC are affected equally by DOP and DOA. The infrared absorptive spectra for the plasticized samples overlap the spectra for PVC and the plasticizer measured separately. For example, these spectra are in the regions of 1730, 1590, 1460, 1340, 1130, and 740 cm^{-1} of DOP and 1730, 1460, 1380, 1180, and 760 cm^{-1} of DOA. It was also noted that the PVC film plasticized by DOP was more absorbent than the PVC film plasticized by DOA in the regions around 1000 cm^{-1}. Figures 2–7, which give more detailed information, may indicate that PVC plasticized with DOP emits slightly more energy than that plasticized with DOA. Also, it may be observed in Figures 3–5 that the emissivities do not increase much in the thinner and thicker film regions.

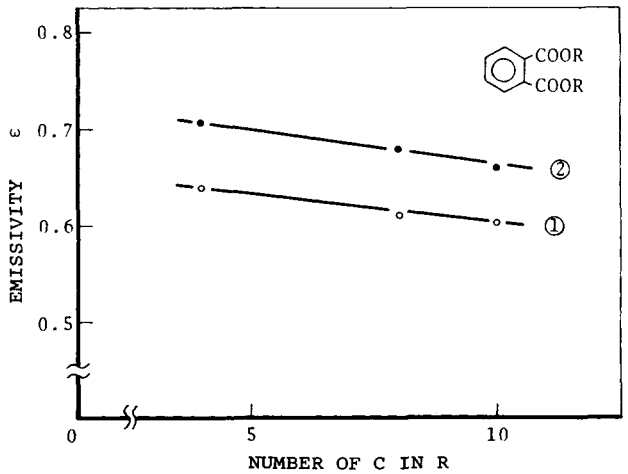


Fig. 9. Decrease in emissivity as function of number of C atoms in R for constant film thickness. Film thickness: ① 60 μ; ② 90 μ.

Next, the effect of the molecular chain length of the plasticizer on the emissivity of plasticized PVC was investigated by use of three plasticizers (DBP, DOP, and DIDP). Figure 8 shows the experimental results. Here, the emissivities for the plasticized PVC film show smaller values with longer molecular sequence length. Such hydrocarbon groups as CH, CH_2, CH_3, and C_2H_5 contribute little to the polymer emissivity as previously reported.[1,4,6,9] This effect is illustrated in Figure 9 as a function of the number of C atoms contained in R for a constant film thickness, which indicates that the emissivity values for the plasticized PVC films decrease gradually with increasing number of C atoms in R.

CONCLUSIONS

Such plasticizers as DOP and DOA when added to PVC shows approximately the same increase in emissivity (about 10–15%). Also, the commercially used plastics with film thickness of 15–30 μ show the highest increase in emissivity ratios.

The emissivity for the plasticized PVC decreases gradually with increasing sequence length in a molecule type such as the phthalic acid plasticizers.

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