

Behaviour of film-forming polymers in a microwave electric field

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The application of a microwave electric field to the formation of polyurethane films supported by a glass substrate has been described previously. The present work concerns the investigation of the separated contributions of a polymer and its solvent during the film formation in microwaves. The measurement technique allows the kinetic formation to be observed by means of a specific infra-red pyrometer which indicates the temperature variation of the film surface when submitted to the electric field inside a waveguide associated to a microwave power generator at 2.45 GHz. Present data show that dielectric relaxation losses of structural elements of the polymers form the dominant heating process in microwave coating.

Keywords Dielectric heating; film-forming polymers; heating kinetics; microwaves; polystyrene; poly(vinyl acetate)

INTRODUCTION

In preceding papers^{1,2} we described the formation of glass supported polyurethane films based on a phenol blocked polyisocyanate (Desmodur AP) and a polyalcohol (Desmophen 800) when submitted to a microwave electric field, at 2.45 GHz in a waveguide. The film formation was observed through an aperture made in the top wall of the waveguide, by means of an infra-red pyrometer (3.45 μm) recording the temperature-time variation curves. These studies have shown the possibility of obtaining organic coating films from prepolymer solutions subjected to a microwave electric field. Moreover, it was observed that the film-forming reaction in microwaves between blocked isocyanate functions in Desmodur AP and alcohol functions in Desmophen 800 can occur for temperatures which are lower than that generally used with the conventional thermal systems. This leads to better efficiency in the energy transfer of the material. Nevertheless, in the complete estimation of the film formation process, the thermal contribution of both the solvent and the substrate has to be considered and it has not yet been possible to determine their exact respective contribution in the reaction development.

The dielectric losses of solvents associated with dipolar molecule orientation in the microwave field often appeared as a dominant parameter which strongly influences the dielectric heating kinetics of polar macromolecules and become the main heating factor when a non-polar polymer is dissolved in a polar solvent. Moreover, chemical reactions of film hardening if present could also influence the whole formation process.

Of course, the literature on dielectric absorption of polar molecules and of polymers is very extensive³⁻⁵, but most of the data are reported for frequencies (up to some megahertz) much lower than microwaves (ca. 0.9 to 300 GHz). For instance, Reddish^{6,7} or Ishida⁸ published surfaces of dielectric dispersion or adsorption in polymers, showing ϵ' and ϵ'' variations as functions of

temperature and frequency, but only up to 1 MHz. By this method, polyvinylacetate was studied by Ishida and Yamafuji⁹, and Mikhailov's papers on poly(vinylacetate) or styrene copolymers¹⁰⁻¹² report low frequency studies, up to 100 MHz. Furthermore, no reference exists on the thermal evolution of dielectric constants, and especially ϵ'' , when materials are heated by microwaves, at 2.45 GHz. Moreover, no data are available, related to polymer solutions considered as a whole, a complex and evolving material when submitted to microwave heating.

The present work is devoted to the investigation of the separate contribution of a polymer and its solvent, respectively, when coating a substrate without dielectric losses (and thus thermally inert in a microwave field) which is submitted to a 2.45 GHz electric field by means of film-forming polymer solutions without any chemical reaction. The microwave power scattered inside the sample and the resulting temperature variation of the film under formation are a function of the dielectric losses and of the electric field strength within the material.

EXPERIMENTAL

Materials

In order to cancel the effect of the substrate on which the film-forming material is spread, the substrate was made of a hollowed PTFE plate, in which the polymer solution was poured. PTFE is a non-polar material, without dielectric losses; thus, its contribution to microwave heating is negligible, when used as a substrate.

Each sample bearer has the same size, including the hollow in the PTFE plate, and the volume of solution was measured by means of a pipette. The studied samples were then identical in shape and volume, so that the filling factor of the microwave cavity only varies as a function of the complex dielectric constant of the studied solution.

Two series of polymers were investigated: poly(vinyl acetate) (PVAC) as a polar molecule with high dielectric

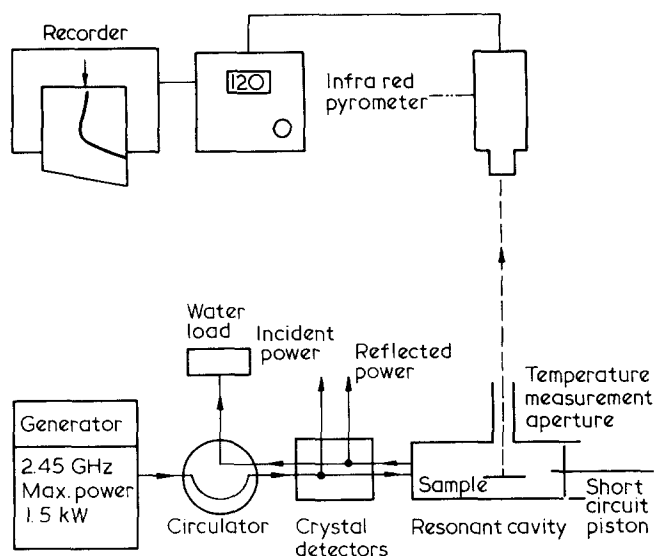


Figure 1 Scheme of the experimental set

losses, and polystyrene, a non polar polymer with low dielectric losses. Both series were dissolved into three solvents: dimethylformamide (DMF), a very polar solvent, benzene, a non polar solvent, and methylethylketone (MEK) with a medium polarity. For each polymer-solvent pair, two concentrations were used: 10% and 20% in weight, i.e. 12 samples in all.

Experimental

The experimental set-up was almost the same as that used to study the formation of polyurethane films. However, taking into account the low dielectric loss level both in PTFE and in some of the studied solutions, a resonant cavity containing the heated sample was used to increase the field applied to the sample. As shown in Figure 1, the experimental set-up includes: a microwave generator (2.45 GHz, 1.5 kW), a circulator to protect the generator from reflected waves, two crystal detectors to measure the transmitted and reflected power, a tunable resonant cavity, with a wall hole just above the PTFE sample-bearer, in the optical axis of an i.r. pyrometer. The cavity is closed with an adjustable short-circuit, the position of which is tuned for each sample, in order to transfer the maximum of the microwave energy to the film-forming material.

The 3.43 μm settled i.r. pyrometer continuously measures the surface temperature of the organic film and is connected to a recorder which is run at the same time as the microwave generator.

The first step of film formation is the evaporation of solvent, and the presence of substantial quantities of solvent vapour in the optical path of the pyrometer could affect the reading. However, no effect was really detected (probably because the great dilution of solvent molecules), except for DMF solutions, related to the liquid DMF condensation in the path, which caused a shaking of the recorder pen. So we consider the maxima envelope of the recorded curve as the actual temperature/time variation. For a given incident power, the recorded curve of temperature vs. time was a characteristic of the dielectric losses of the heated film.

RESULTS

Each solution was subjected to different levels of incident microwave power, between 100 and 700 watts. Most of the temperature vs. time curves reveal a fast temperature increase at the beginning, due to the mixture heating. The second effect, which is most marked for MEK solutions (Figures 2.2, 2.5 and 3.5), and may be discerned for benzene solutions (Figures 2.1 and 2.4), is the presence of plateaux or points of inflection in the 70°–90° region, due to the evaporation of the largest part of solvents, and only visible if the incident power level is not too much higher, related to the evaporation rate of solvent.

The third part of the curve often shows a peak which will be discussed later. The temperature then decreases and reaches a steady value, which is a function of both the incident power and the polymer nature, according to its dielectric losses and to convection heat losses. When the incident power level is high, a thermal equilibrium cannot be obtained, and temperature rises again as a function of the dielectric losses in polymer (Figure 2.1 at 500 and 700 W, Figure 2.2 at 700 W, Figure 2.4 at 300 W, Figure 3.2 at 700 W). Poly(vinyl acetate) illustrates such a behaviour, i.e. the polymer is able to heat by itself because of its high losses. Moreover, the temperatures reached by PVAC solutions were generally higher than those for polystyrene solutions, at the same power density.

The influence of the solvent nature clearly appears in the case of polystyrene, which is a non polar system (Figure 3). In general, the higher the solvent polarity and dielectric losses, the higher the heating rates and final temperatures, except for PVAC solutions in MEK (Figures 2.2 and 2.5) when compared to benzene solutions of the same polymer. DMF solutions are heated quickly at high temperatures (Figures 2.3 and 2.6), but heating is delayed a little after microwave application. Except for PVAC solutions in DMF, an increased concentration of polymer enhanced the phenomenon, considering either the heating rate of the final temperature, and even in the case of polystyrene (non polar polymer) solutions in DMF (polar solvent) whereas the relative amount of polar material (the solvent in this case) was decreasing. These peculiar points will be discussed later.

DISCUSSION

The behaviour of polystyrene, as a non polar polymer, was easier to explain than the behaviour of PVAC, for the dielectric losses of polystyrene solutions were essentially due to the solvent. Therefore, a benzene solution of polystyrene was quite inert; an MEK solution was slightly heated by means of the solvent dielectric losses, and a thermal steady state was found according to the dielectric losses in polymer at the final temperature; a DMF solution showed the same behaviour, enhanced by the high dielectric losses in DMF. However, the phenomenon was also enhanced by a higher polystyrene concentration, though the concentration of 'active' compound (DMF) and the dielectric losses were lower. In fact, DMF must be considered as an efficient energy transfer agent, but being evaporated during microwave irradiation; the higher the concentration the thicker the solid residue, so that it absorbed much more energy, and the final temperature was higher.

PVAC is a polar material, the dielectric losses of which are to be added to those of the solvent. In a benzene

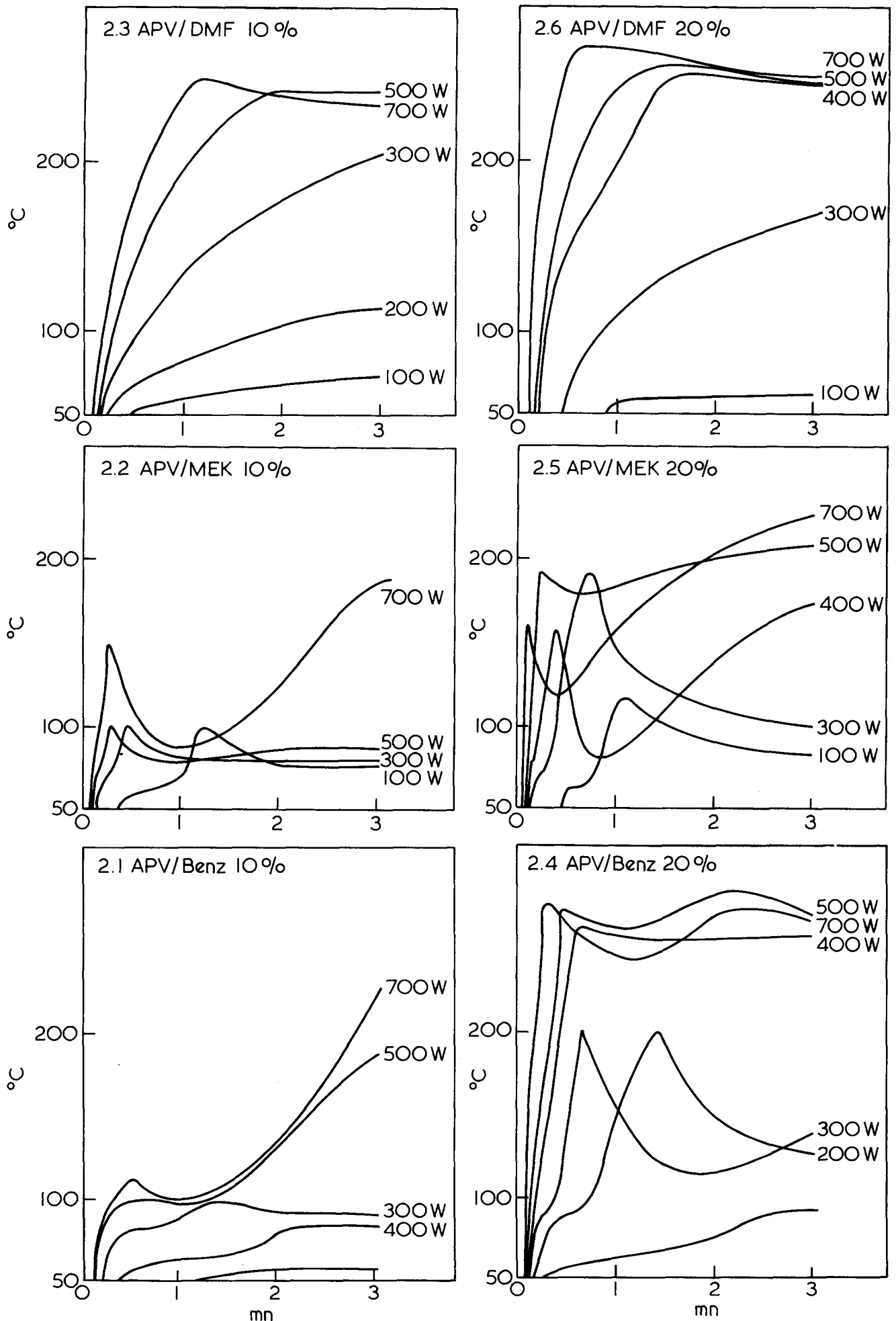


Figure 2 Heating kinetics of poly(vinyl acetate) solutions

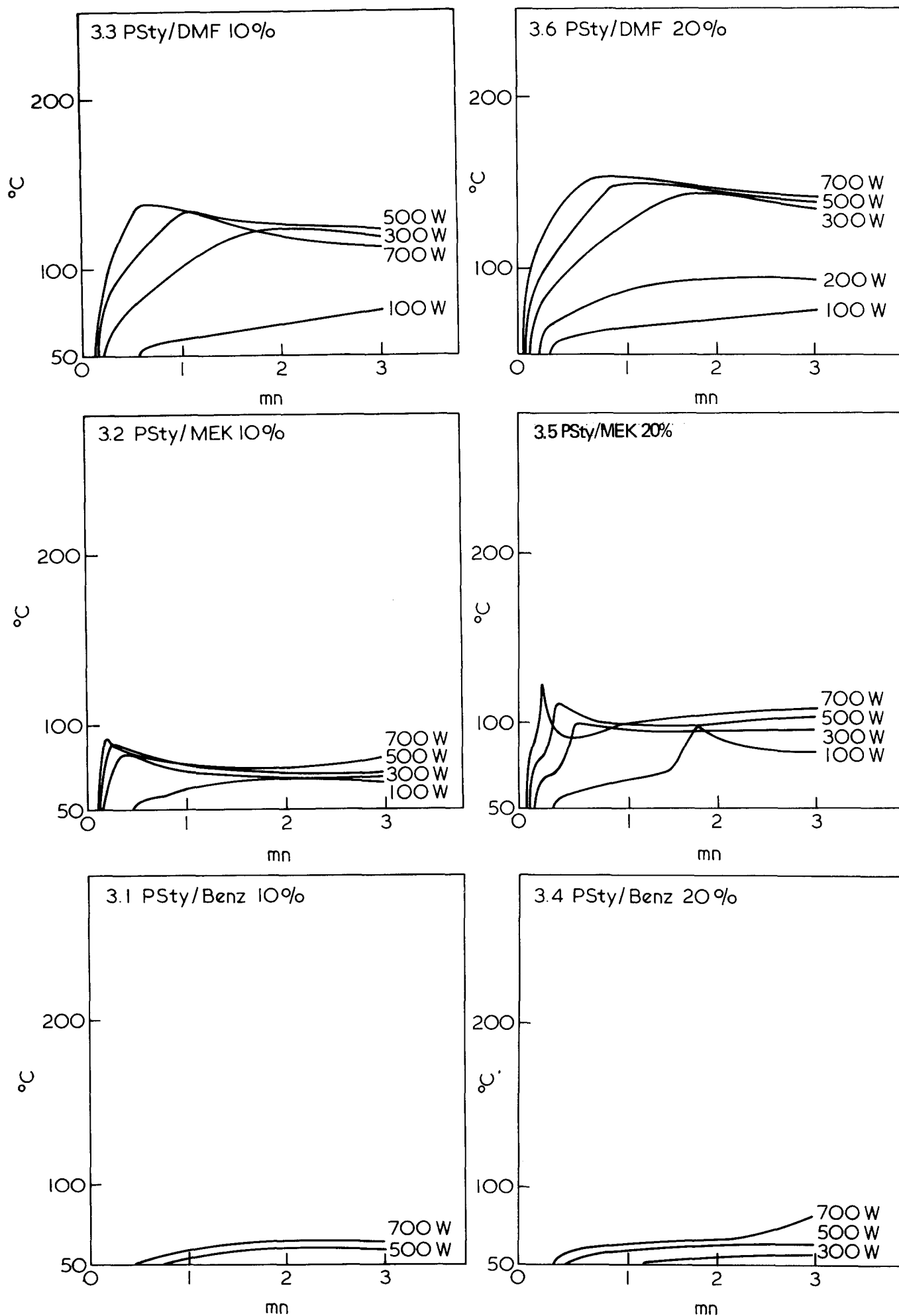


Figure 3 Heating kinetics of polystyrene solutions

solution, PVAC is the main heating agent: for a high microwave power level, a thermal equilibrium was obtained at high temperature (Figure 2.4), or sometimes no thermal equilibrium was reached (Figure 2.1). MEK solutions, however, showed a lower effect of microwaves: some interactions between the two compounds probably constricted the electrical orientation of polar groups, so that the resulting thermal effect was decreased compared to a benzenic solvent likewise 20% solutions in DMF were less sensitive to microwaves than 10% solutions; this effect could be due either to the 'dilution' of the high dielectric losses of solvent by addition of a solute with low dielectric losses, or to interactions between DMF molecules and functional groups in PVAC, preventing its dipolar coupling with the electric field.

In other respects poly(vinyl acetate) might partly be degraded into acetic acid, so that this highly polar molecule could have influenced the related results. Microwaves, however, being a non-ionizing electromagnetic radiation, such a degradative process would only be a thermal one. Considering the very short time of treatment (3 min), no degradation was really observed.

In both cases, polystyrene or PVAC, a maximum can be observed in the temperature vs. time curves, after the plateau or inflection due to solvent evaporation. This peak could be attributed, firstly to solvent retention, either maintaining a level of dielectric losses in the material until the solvent is completely removed, or acting as a plasticizer and allowing the relaxation of polymer polar groups; and secondly to a thermal effect of the rearrangement of molecules during the film formation. Further experiments are necessary to verify these hypotheses.

Consequently, the very different aspect of the temperature vs. time curves obtained with PVAC solutions (Figure 2), compared with those of polystyrene solutions (Figure 3), shows that the nature of the polymer (polar or non polar) is the main factor which governs interactions between the microwave field and polymer solutions. Solvent polarity and its associated dielectric losses, as well as concentration, were secondary factors which control the amplitude of interactions, but did not influence the general aspect of the phenomenon.

CONCLUSION

The thermal behaviour in microwave fields of film-

forming polymer solutions depends on several factors. Besides, the effect of electric field intensity, related to the applied power, the active parameters are the polarities of both polymer and solvent, and of course the solution concentrations. However, the polarities of the polymer and that of the solvent are not independent parameters in controlling the process for polymer-solvent interactions influence the final thermal behaviour of solutions.

This work shows, in contradiction with our previous consideration for the polyurethane film formation on glass substrates^{1,2}, that the polymer nature is a factor which controls the general aspect of the time dependence of film temperature. For a polar polymer, the solvent only amplifies the heating process by means of a thermal impulse given at the beginning of heating and before it is evaporated. Moreover, in the present case, and unlike the polyurethanes studied previously^{1,2}, no curing chemical reaction occurs for the film formation from polystyrene or PVAC solutions. Thus, the dielectric relaxation losses of structural elements in polymers actually are the main parameter in the heating process. Consequently, a study of the dielectric properties of polymers and prepolymers, and of their evolution as a function of the coating application parameters, is always necessary to optimize the deposition of organic coatings by means of microwave electric fields.

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