

Physical and Relaxation Properties of Flame-Sprayed Ethylene-Methacrylic Acid Copolymer

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A range of physical and chemical properties of flame-sprayed ethylene-methacrylic acid copolymer (EMAA) were assessed, following different processing conditions. Coatings were produced at a range of specific temperatures by varying the propane flow rate and gun traverse rate. The flame spraying process oxidizes the EMAA copolymer during processing, the extent of oxidation increasing with greater deposition temperatures. Coatings were scanned using dielectric relaxation spectroscopy at a frequency range from 10^2 to 10^6 Hz over a temperature interval of -20 to 85°C . The glass transition temperature (usually denoted as the β' relaxation in this system), is attributed to the **microBrownian** motion of long chain segments in the amorphous phase and is found to decrease with increasing deposit temperature. The oxidation process appears to reduce the position of the α' relaxation due to chain scission. The molecular weight for the EMAA powder was reduced from $22,693$ g/mol to 9302 g/mol when deposited at 271°C as shown by gel permeation chromatography. Despite the decrease in chain length, the activation energies for β' relaxation increased with increasing coating temperatures. This is attributed to the increased polarity of the oxidized coatings resulting in greater intermolecular association, which outweighs the decreased chain length.

1. INTRODUCTION

Many techniques have been used to characterize the structure and properties of ethylene-methacrylic acid copolymer (EMAA); a polymer that recently has been widely used in a resurgent thermal polymer spray industry (1-3). In addition, the dielectric and mechanical relaxations associated with the glass transition temperature have been well documented for compression molded EMAA and their ionic

salts (4-8). Thermal spraying of polymers represents an alternative method to process polymer powder to produce both polymeric coatings and free-standing forms of great complexity (9, 10). Moreover, thermal spraying allows the coating and repair of large structures such as bridges (11). Such alternative methods of applying barrier coatings are an environmentally attractive alternative to solvent-based paints because of their lack of hazardous chemicals. However, despite extensive use of EMAA copolymers in the field and in laboratory studies, most work to date has mainly involved study of mechanical and adhesion properties

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as well as processing effects (12, 13). Much less has been reported on the effect of the rapid exposure of these organic molecules to a high temperature flame (in the presence of oxygen) and the resulting effects on the polymer chains. This paper is principally concerned with determining the dielectric and other related physical and chemical properties of flame-sprayed EMAA copolymer.

Recent dielectric relaxation spectroscopy (DRS) and dynamic mechanical thermal analysis (DMTA) studies confirm two different relaxations (β' and γ) for pressed EMAA copolymer films (7, 8). The β' relaxation is ascribed to a micro-Brownian molecular motion (glass transition) of long segments within the amorphous phase which involves the breaking and reforming of interchain hydrogen bonds (4-8). Differential scanning calorimetry (DSC) studies have shown that at acid contents less than 8 mole %, the copolymer is partly crystalline (1, 5). The literature also suggests that the acid groups are excluded from the crystalline region and reside in the amorphous phase (1, 14). Temperature controlled, polarized infrared studies have shown that the carboxylic acid groups are hydrogen bonded together to form interchain dimers below the glass transition temperature (15) and a monomer-dimer equilibrium was proposed between the acid groups even at temperatures greater than the T_g (16). The γ transition in EMAA is a secondary relaxation comprised of two overlapping peaks at -163 and -129°C (17). It was proposed that the -163°C peak is due to motion of lattice defects within the crystalline phase and the -129°C peak arises from local motions within the amorphous polyethylene phase (18).

The object of this paper is to determine whether the flame-spraying process affects the properties of the EMAA copolymer. In the dielectric analysis, attention will be focused on the β' relaxation. Coatings were produced at various temperatures by altering the process parameters and the results compared to compression molded EMAA samples.

2. EXPERIMENTAL

2.1 Materials

The EMAA powder was received from Plastic Flame-coat Systems, Inc. (Big Spring, Tex.). The copolymer contains approximately 4 mole % methacrylic acid units and has a melt flow index of 32 g/10 min. Powder size distributions were obtained using MicroTrac Powder Analysis (Leeds and Northrup Instruments, North

Wales, Pa.). The average size, assuming a spherical shape factor, was 140 pm with a standard deviation of 70 pm. Ninety percent of the powders were less than 220 pm.

2.2 Flame Spraying

The combustion torch used in this study is the Powder Pistol 124 (PFS Thermoplastics, Big Spring, Tex.), which is connected to a fluidized bed powder feeder. Propane and compressed air are used as the fuel and oxidant for the combustion process. The compressed air supply also provides air for powder transport through the flame and to fluidize the powder. Polymer powder is axially fed into the combustion zone via compressed air. The polymer particulates are propelled through the flame, where upon melting they become droplets and are transported to the substrate. As the molten particles impinge on the substrate, the well-heated particles will deform and solidify, forming an interlaced network of splats. A Teflon pan was used as the substrate to facilitate easy removal of the coating (Teflon is a trademark of the DuPont Company). Coatings measured approximately 2 mm in thickness. The spray parameters are listed in Table 1. Mass-flow controllers were used to precisely control and monitor each gas flow rate. The propane flow rate and traverse rate were varied to produce coatings at different temperatures. An infrared pyrometer measured the temperature of the deposit immediately after spraying and these temperatures are indicated in column 1 of Table 2.

2.3 Specimens

The coatings were removed from the Teflon coated pan when they cooled to room temperature. Samples for dielectric testing were produced by hot-pressing the coatings at 150°C with a force of 0.5-1.0 kN for 30

Table 1. Parameters Used to Deposit Coatings.

Spray Parameter	Value
Propane flow rate	3.1-7.1 l/min
Propane tank pressure	345 kPa
Fluidized bed air flow rate	24 l/min
Combustion air flow rate	23 l/min
Carrier air flow rate	49 l/min
Compressed air pressure	690 kPa
Stand-off distance	30-45 cm
Traverse rate	5-15 cm/sec
Substrate preheat temperature	66°C

Table 2. Dielectric Relaxation Properties of EMAA Coatings.

EMAA Film	M_w	β' Peak Temp (°C)			E_a (kJ/mol)
		1 kHz	10 kHz	100 kHz	
Pressed - 150°C	22,693	46	61	73	153
Sprayed - 216°C	11,452	43	55	67	165
Sprayed - 271°C	9,302	32	43	55	177
Sprayed - 340°C	—	28	37	49	184
Sprayed - 400°C	—	30	40	49	210

seconds to achieve a film thickness of 500 μm . Films from neat powder were also produced by compression molding the EMAA powder at 150°C with a force of 5 kN for 5 minutes. The films were allowed to cool overnight and cut into 25 cm diameter samples.

Specimens for FTIR spectroscopy were obtained from the original flame-sprayed coating. These samples were pressed at 150°C with a high force of 20 kN for five minutes to obtain sufficiently thin films approximately 20 μm in thickness. Similarly, neat powder was pressed with a force of 20 kN at 150°C for five minutes. No other thermal treatment was applied to the EMAA samples prior to testing. It was assumed, because of the relatively mild nature of the compression molding required, that the state of the polymer was changed little by pressing compared with the effects to the material due to spraying.

2.4 Measurements

Gel permeation chromatography was conducted on the pressed EMAA powder as well as on flame-sprayed EMAA coatings deposited at 216°C and 271°C. A C-045 PLGEL column was used in conjunction with an RI detector (Waters R-401) and a UV/VIS detector (Perkin Elmer LC-55B). The column was calibrated using polystyrene standards with the following molecular weights: 2430k, 1100k, 505k, 180k, 22k, 2450, and 1700. The solvent in the column was tetrahydrofuran (THF) at 5.5 MPa. Samples were prepared by refluxing the EMAA copolymer in THF and 100 μl injection volumes were used.

Variable frequency dielectric relaxation spectroscopy (DRS) was conducted on a Hewlett Packard 4824A

Digibridge. The technique involves measuring the dielectric capacitance and loss as a function of frequency (10^2 – 10^6 Hz). Details of the measurement are described elsewhere (19). The polymer film was placed between two electrodes measuring 15 and 23 cm in a three terminal type cell. Conductive vacuum grease was used to ensure good electrical contact between the polymer sample and the two electrodes. The cell was placed in a temperature controlled, environmental oven, enabling measurements to be taken over the temperature range of -20 to 85 controlled to $\pm 1^\circ\text{C}$. Windows-based software (NovoControl, Germany) was used for temperature control, to operate the dielectric bridge, and for data collection and manipulation.

Fourier transform infrared spectroscopy (FTIR) was conducted on a Perkin Elmer 1600 instrument. Grams Analysis 1600 software controlled the operation of the instrument and was used for peak analysis. Spectra were recorded by averaging 16 scans in transmission mode with a resolution of 16 cm^{-1} .

3. RESULTS

3.1 Gel Permeation Chromatography

The average molecular weights of the pressed powder coating and of the flame-sprayed coatings are listed in Table 2. The average molecular weight for the pressed EMAA powder is 22,693. Chain scission occurred during the flame-spraying process as evident by the reduced molecular weight when deposited at 216°C (11,452) and at 271°C (9302). The coating deposited at 400°C remained insoluble in THF, indicating that the material was crosslinked to some degree.

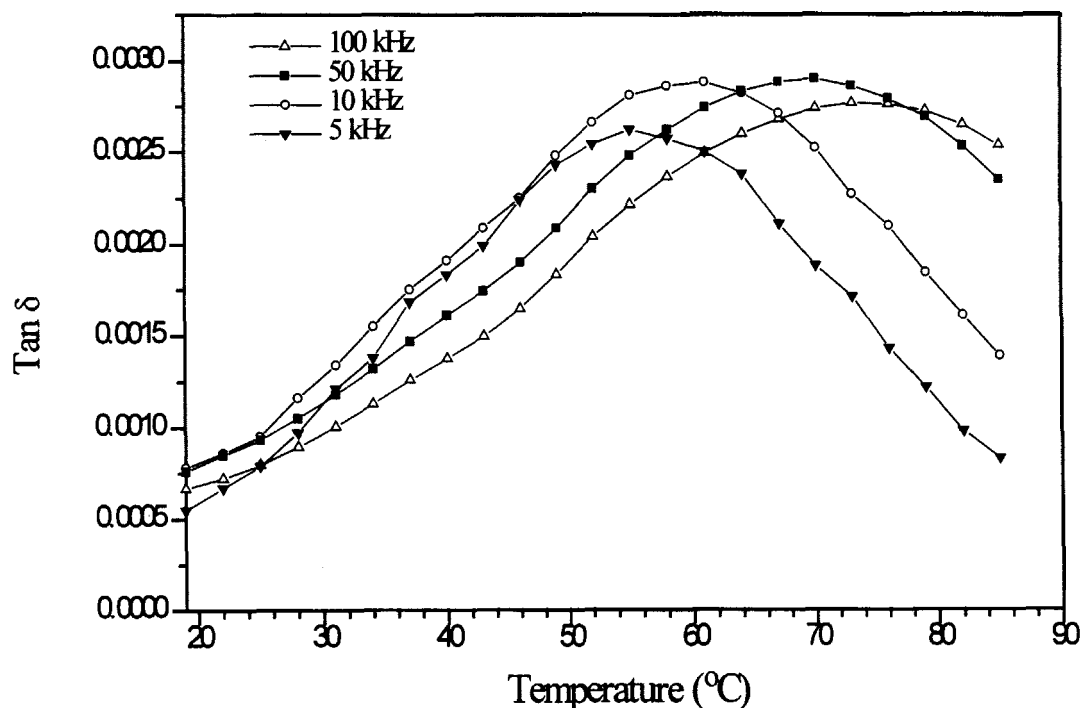


Fig. 1. Temperature dependence of $\tan \delta$ for various frequencies (EMAA powder).

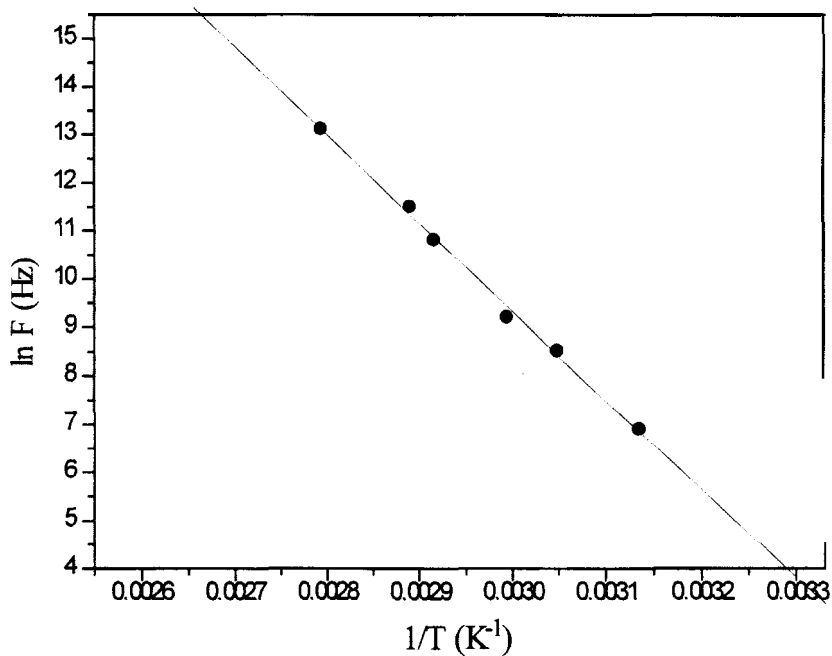


Fig. 2. Temperature dependence of loss peaks for pressed EMAA powder.

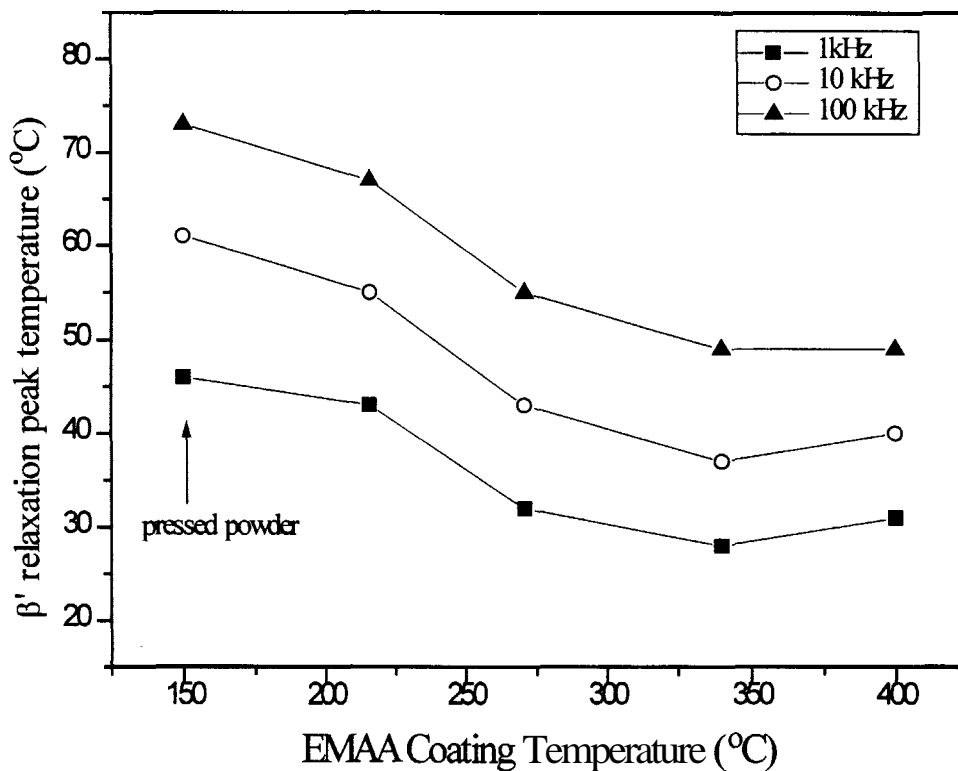


Fig. 3. Relaxation temperatures for sprayed EMAA samples.

3.2 Dielectric Relaxation Spectroscopy

Figure 1 shows the temperature dependence of $\tan \delta$ for the pressed EMAA powder sample. $\tan \delta$ is calculated from:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (1)$$

where ϵ'' represents the dielectric loss and ϵ' the dielectric permittivity. The location of the frequency maximum represents the β' relaxation, ascribed to the micro-Brownian molecular motion of long chain segments (4-8). This transition is reflective of the glass transition temperature of the amorphous region with randomly distributed ethylene and methacrylic acid

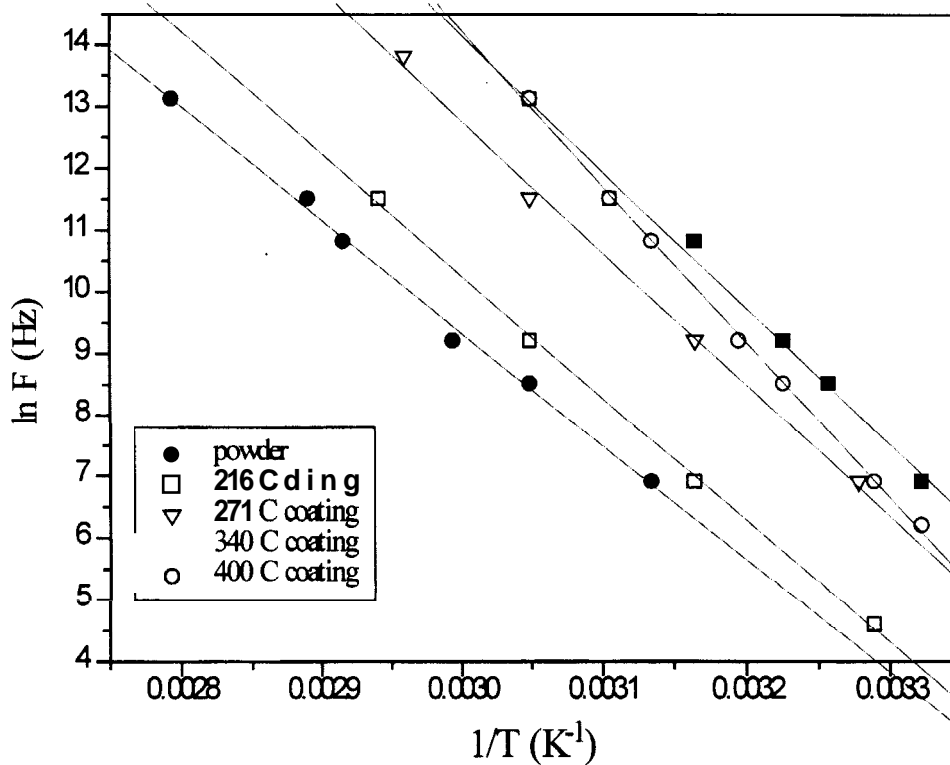


Fig. 4. Plots used to calculate Arrhenius activation energies for EMAA samples.

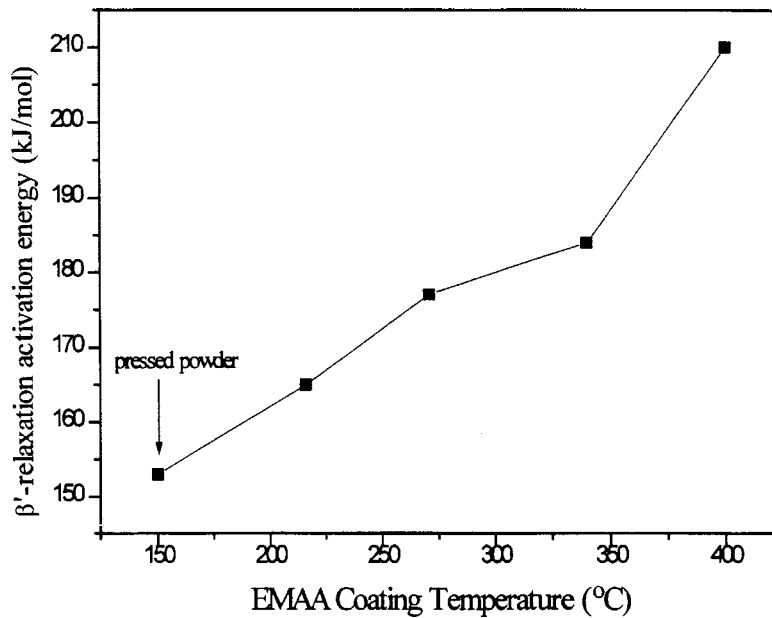


Fig. 5. Activation energies for β' relaxation

comonomer units (1). The β' relaxation temperature increases with increasing frequency, as expected, producing the temperature-frequency locus shown in Fig. 1. The relaxation occurs at 55°C for 5 kHz measurement and increases to 73°C at a frequency of 100 kHz. The temperature dependence of the loss peaks show an Arrhenius dependence;

$$f_m = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where f_m represents frequency, A is the pre-exponential factor and E_a is the energy barrier to motion. Figure 2 plots the logarithm of frequency against the reciprocal temperature. The activation energy for the

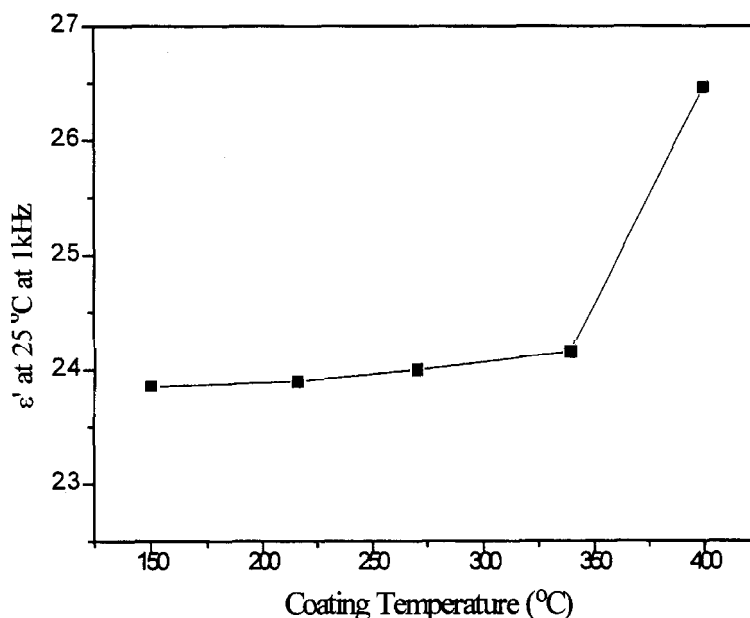


Fig. 6. Dielectric constant measured \pm 1kHz at 25°C.

β' relaxation is 153 kJ/mol for the pressed EMAA powder. Since the glass transition temperature is expected to show a free volume non-linear dependency, the linearity of the curve in Fig. 2 and use of an Arrhenius equation needs to be justified. The linearity probably arises because of the limited range of frequencies (100 to 106 Hz) available using our DRS equipment. If a much broader frequency range was available a WLF-like temperature-frequency locus would be expected (20). An activation energy determined by the Arrhenius relation can be used for the purpose of comparison with other EMAA samples deposited at different coating temperatures.

Figure 3 plots the temperature location of the β' relaxation for the flame-sprayed coatings as well as the pressed powder coating at a range of frequencies. For each applied frequency, the β' relaxation temperature decreases with increasing coating deposition temperature with a slight increase for 400°C deposited coatings. Arrhenius activation energies can be calculated for each sprayed coating from the plots in Fig. 4 and are shown in Table 2. The activation energies associated with the β' relaxation increase with increasing EMAA coating temperature, Fig. 5. The coating sprayed at 400°C has the highest measured activation energy at 210 kJ/mol.

Figure 6 plots the dielectric constant (ϵ') measured at 25°C at a frequency of 10^3 Hz and allows comparison of polarity of the various sprayed polymers at a constant temperature and frequency. The dielectric constant for the EMAA pressed powder was measured at 2.38. The permittivity essentially remained constant for the flame-sprayed samples deposited at temperatures less than 340°C. Temperatures greater than 340°C produced a significant rise in the dielectric permittivity, as observed in the coating deposited at 400°C (measuring 2.65).

3.3 FTIR Spectroscopy

The FTIR spectra for the pressed powder and flame-sprayed coatings are shown in Fig. 7a. Very little distinction can be made between the starting powder and the flame-sprayed coating deposited when at the most extreme temperature, 400°C. The assignment of the most prominent absorbances are as follows. The band at 720 cm^{-1} (a) contains both amorphous and crystalline components as a result of CH_2 rocking modes, whilst the band at 1380 cm^{-1} (b) arises from symmetric CH_3 deformation (21). The band at 1464 cm^{-1} (c) is due to the CH_2 deformation while the carbonyl stretching absorption was found to occur at 1700 cm^{-1} for all EMAA specimens, instead of the 1750 cm^{-1} absorption for free carboxylic acid groups. This absorption shift is due to the fact that most of the $-\text{COOH}$ groups are linked to neighboring chains containing $-\text{COOH}$ groups in the form of hydrogen-bonded dimers (22). It is estimated that at room temperature less than 1% of the carboxylic groups are free (15). This coupling of carboxylic groups is responsible for lowering the absorption frequency. Examining the carbonyl stretching absorption in greater detail, Fig. 7b reveals a broader peak at 1700 cm^{-1} for the coating sprayed at 400°C. A shoulder can be observed at the high frequency tail of the band in comparison to the pressed EMAA powder.

The carbonyl absorption at 1700 cm^{-1} was integrated and normalized with respect to the integrated CH_2 absorption at 1464 cm^{-1} . This ratio denoted the "carbonyl index" represents a quantitative assessment of the concentration of carbonyl groups present in the polymer structure, as judged by this method. A higher carbonyl index correlates to a more oxidized polymer than a lower carbonyl index. As shown in Fig. 8, the carbonyl index increases with increasing coating temperature.

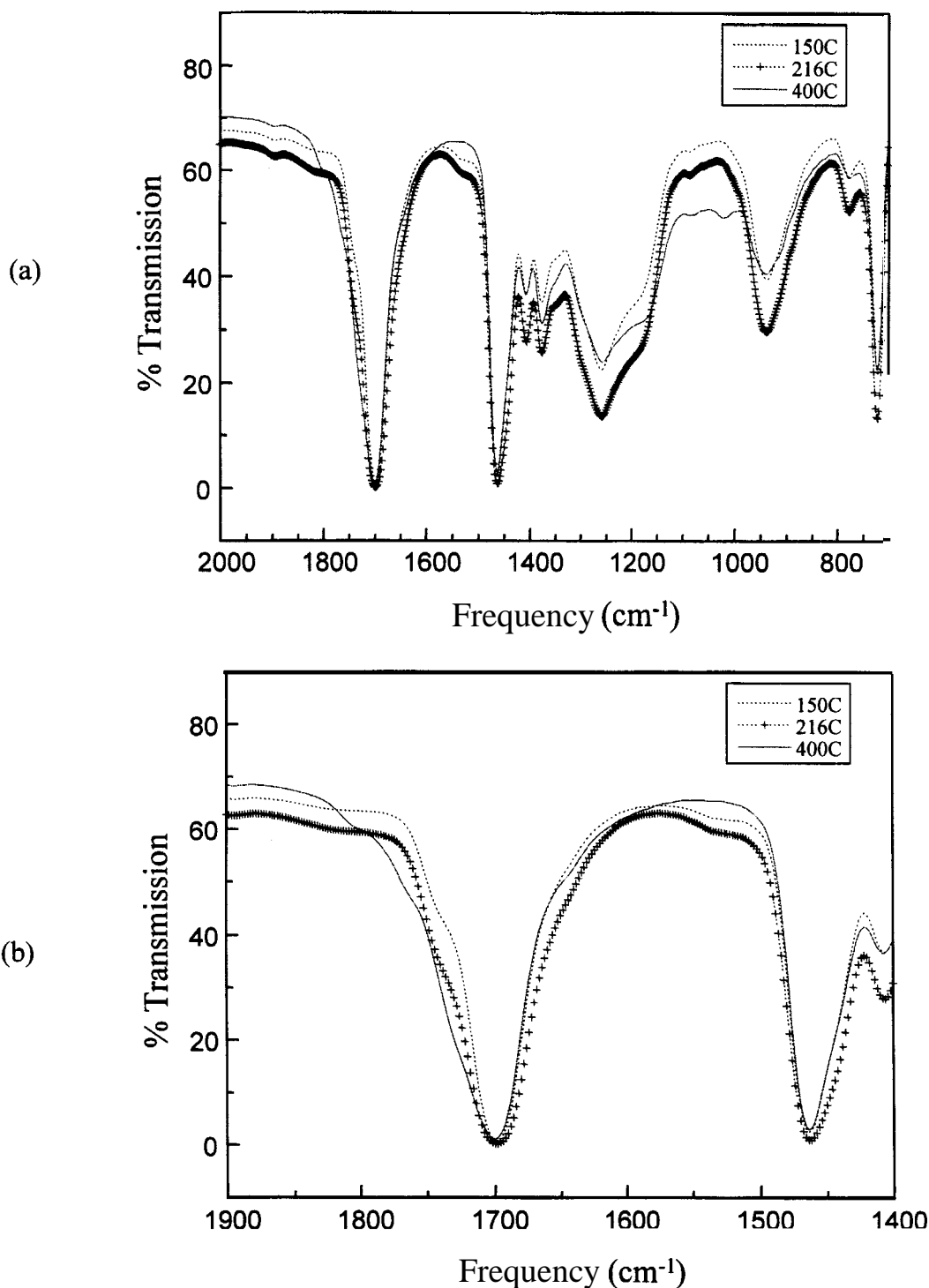


Fig. 7. FTIR spectra of pressed EMAA powder, sprayed at 216°C and sprayed \pm 400°C: a) from 2000 to 700 cm^{-1} and b) from 1900 to 1400 cm^{-1} .

4. DISCUSSION

Polymer coatings were flame-sprayed at successively higher temperatures by increasing the propane flow rate and decreasing the gun traverse speed. The particle residence time and, thus, thermal heating within the flame increases with increasing propane flow rate

(23). Coatings deposited at temperatures lower than 216°C did not show any visible signs of degradation. However, the EMAA coating produced at 271°C contained bubbles, approximately 300 μm in diameter and the films appeared yellow in color. Coatings deposited at 340°C and 400°C were further degraded, yielding larger bubbles and a darker color. Coating dis-

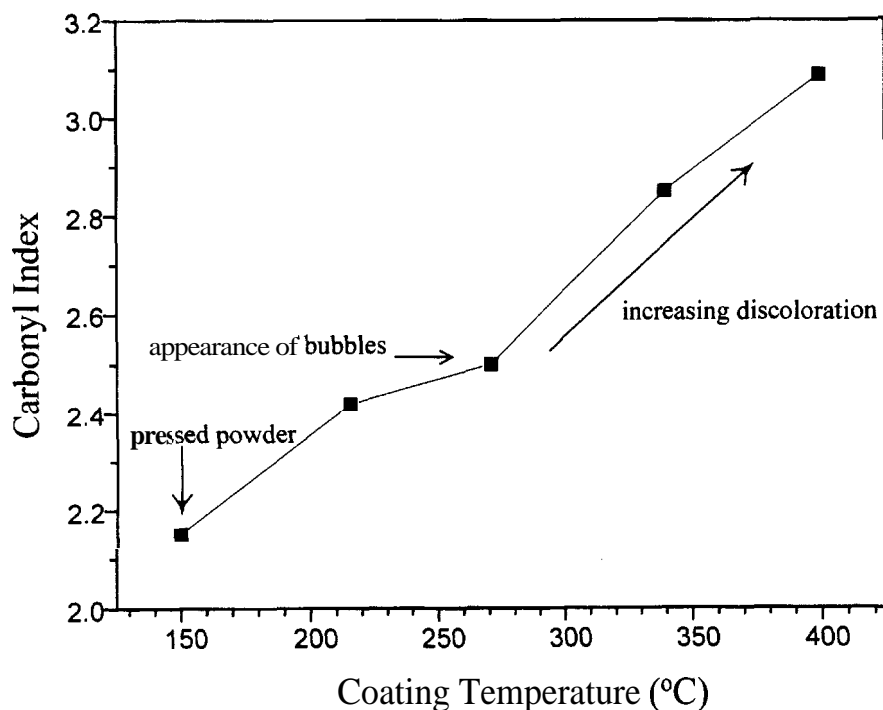


Fig. 8. Integrated carbonyl peak at 1700 cm^{-1} ratioed to CH_2 peak at 1464 cm^{-1} .

coloration has been attributed to an increase in oxidation products as a result of thermal-oxidation (24). It is not known whether there is a corresponding increase in conjugated double bonds.

A higher carbonyl index (ratioed integrated carbonyl absorption at 1700 cm^{-1} to the integrated CH_2 absorption at 1464 cm^{-1}) supports the increased oxidation at higher coating temperatures. The shoulder at the high frequency tail of the 1700 cm^{-1} carbonyl absorption may arise from increased amounts of free $-\text{COOH}$. It is believed that the bubbles in the flame-sprayed EMAA specimens are produced from the degradation of the methacrylic acid groups. Low density polyethylene powder was sprayed at the same temperatures as the EMAA powder, producing coatings with increasing discoloration, but without the appearance of bubbles. The precise oxidation mechanism of EMAA copolymer will be the topic for a future publication.

Although the dielectric constant essentially remained constant for coatings deposited at temperatures lower than 340°C , the β' relaxation temperature depends on the processing conditions that govern the final temperature of the coating. The β' relaxation decreased as the coating temperature increased. However, at 400°C , the data shows a slight increase in the relaxation temperature.

Activation energies for the β' transition increased from the 150°C pressed-powder coating to the 400°C flame-sprayed coating. A higher activation energy is normally indicative of longer range or increasingly coupled motion (19). However, it is known from GPC that there is a decrease in the average chain molecular weight with increasing coating temperature. While

the increasing free volume resulting from lower molecular weight could be responsible for the lower β' relaxations, it does not explain the higher activation energies for flame-sprayed EMAA copolymer samples. The higher activation energies for the β' relaxation may possibly be explained on the basis of an increased amount of polar groups incorporated into the polymer structure during spraying. The higher the coating temperature, the more susceptible the polymer is to thermal oxidation; hence more polar groups are present (24). The FTIR spectra on flame-sprayed EMAA reveal higher carbonyl concentrations with increasing coating temperatures. These polar groups may link neighboring chains through secondary intermolecular bonding interactions, increasing the activation energy for β' relaxation motion although the actual glass transition is little changed. The constancy of the dielectric constant at room temperature does not necessarily indicate that the technique is insensitive to increases in dipolar concentration, such as by oxidation. The dielectric constant is a complex function of the molecular mobility (which is limited at 25°C , below T_g) and is also dependent on chain conformation and possible cancellation of dipoles due to molecular shape of the chains and possible dipolar interaction. A better estimation of dipolar concentration is often obtained by determining the dipolar strength of a relaxation, $\Delta\epsilon$, where $\Delta\epsilon = \epsilon_r - \epsilon_\infty$ where ϵ_r is the relaxed (low frequency limit) of the dielectric constant and ϵ_∞ is the unrelaxed and numerically low value of the dielectric constant at the high frequency limit. Moreover, $\Delta\epsilon$ is normally obtained by fitting semi-empirical relaxation functions such as the Havriliak-Negami functions to ϵ' or ϵ'' as a

function of frequency (19). However, in this work, β' peaks could only be observed by temperature scanning. The β' peaks were not seen during isothermal, frequency scans because of the high ionic conductivity and relatively low relaxation strength of the low concentration of dipoles in the amorphous region. In any event, by using ϵ' at one temperature and frequency, we were attempting to find a simple, readily measurable parameter to quantify polarity. In this instance, ϵ' does not appear to be so sensitive other than under the most degradative conditions.

Although it was determined that the average molecular weight decreased upon spraying the EMAA powder at 216°C, it was previously determined that optimum mechanical properties were obtained at this temperature (13). It is necessary to fully coalesce the impinging polymer droplets to form an equilibrated structure to obtain coatings with maximum tensile strength and hardness.

In addition to chain scission, cross-linking reactions may also result from thermal-oxidation (24). Each of the flame-sprayed coatings was dissolved in THF after being refluxed for 10 min, except for the 400°C coating. After two hours, most of the 400°C coating remained insoluble, suggesting a degraded but cross-linked structure. This may explain the slight increase in the β' relaxation temperature in comparison to the 340°C coating. The increased dielectric constant at 400°C in comparison to that at 340°C reveals a greater incorporation of polar groups within the polymer architecture,

5. CONCLUSIONS

This study of flame-sprayed EMAA powder has revealed the following conclusions:

1. The flame spraying process oxidizes the EMAA copolymer during processing. The extent of oxidation increases with increasing deposition temperatures.
2. The flame spraying process reduces the molecular weight of the copolymer. The molecular weight for the powder was reduced from 22,693 g/mol to 9302 g/mol when deposited at 271°C. Degradation to the coatings was visually observed at temperatures higher than 271°C in the form of coating discoloration and trapped gaseous bubbles within the coating.
3. The β' relaxation temperature decreased with increasing coating temperatures as a result of chain scission. The temperature dependence of the $\tan \delta$ peaks show an Arrhenius dependence. Activation energies for the β' relaxation increased with increasing deposition temperatures. It is assumed that the higher concentration of polar groups from the thermal oxidation process is responsible for increasing the β' activation energy.

4. The flame-spraying process does not appreciably change the dielectric constant of the EMAA copolymer when processed below 340°C and indicates it may not be a suitable parameter to quantify oxidation.

6. ACKNOWLEDGMENTS

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