

Comparison between the Effects of Alcohols and Diols on Polymethyl-methacrylate And Polyacrylamide with Positron Annihilation Lifetime and Electric Conductivity Measurements

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ABSTRACT: Comparison between the effect of alcohols and diols on poly(methylmethacrylate) (PMMA) and polyacrylamide (PAA) was investigated by positron annihilation lifetime (PAL) spectroscopy and electric conductivity measurements. The samples were prepared by adding alcohols, such as ethanol (E), isopropyl alcohol (P), and butyl alcohol (B), and diols, such as ethanediol (E_{1,2}), isopropanediol (P_{1,2}), and butanediol (B_{1,2}, B_{1,3}, B_{1,4}). The o-Ps lifetime values (τ_3) of PMMA-alcohol or PMMA-diol composites are shorter than the τ_3 value of the virgin PMMA, whereas the τ_3 values of PAA-alcohol or PAA-diol composites fluctuate above and below the corresponding value of virgin PAA. On the other

hand, a significant increase was observed in the o-Ps intensities (I_3) of both PMMA and PAA composites with added alcohols and diols compared with pure PMMA and PAA. The electric conductivity (σ) also increased for both PMMA and PAA composites with added alcohols and diols compared with the virgin PMMA or PAA polymer. A correlation was found between positron annihilation lifetime parameters and electric conductivity of PAA composites. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3078–3083, 2003

Key words: polymerization; composites; oligomers

INTRODUCTION

Positron annihilation lifetime (PAL) spectroscopy has emerged as an effective method for characterization and investigation of the microstructure of polymer matrix and fillers composites.¹ Maurer et al.² measured the PAL spectra of glass bead-filled high-density polyethylene (HDPE), with a glass content ranging from 0 to 50% by volume. A composite model for positron annihilation was proposed to account for the observed changes in the relative intensities with increasing amount of filler. Wang et al.³ measured the positron lifetime as a function of volume fraction of CaCO₃ particles on HDPE-CaCO₃ polymer composites with and without addition of a coupling agent. They found that the positron lifetime (τ_2) and its intensity (I_2) are strongly affected by the structure of the interface layer between the CaCO₃ particle and HDPE matrix. Yan Fengyuan et al.⁴ used the PAL spectrum to detect microscopic imperfections in graphite-poly(tetrafluoroethylene) (PTFE) composites in a wide graphite volume content ranging from 0 to 50%. Their results indicated that changes in size and concentration of the microimperfections of graphite-PTFE composites are related to the increase of graphite volume content, whereas the crystallinity of PTFE shows a tendency to increase. Madani et al.⁵ used PAL spectroscopy to study

the microstructure of PTFE-silica composites. The long lifetime component τ_2 is ascribed to silica particles occupying the large free volume cavities in the PTFE-silica composites. John et al.⁶ investigated composites of carbon fibers and epoxy polymers and found a relationship between fiber fractions by PAL spectroscopy and between apparent volume and weight fractions by density measurements. The room-temperature electrical conductivity of HDPE-carbon black (CB) switching composites as a function of the conductivity of the filler (CB) content was studied by Patnaik et al.⁷ using PAL spectroscopy. The CB imparted high conductivity to its composites starting at a low level of loading.

In the present work, the PAL technique is used to monitor the changes in the combination of alcohols and diols with both polymethylmethacrylate (PMMA) and polyacrylamide (PAA) to form polymer composites. Alcohols such as ethanol (E), isopropyl alcohol (P), and butyl alcohol (B) and diols such as ethanediol (E_{1,2}), isopropanediol (P_{1,2}), and butanediol (B_{1,2}, B_{1,3}, B_{1,4}) are used. Also, a correlation between the macroscopic electric conductivity and microstructure free-volume properties of composites are established.

Experimental

Preparation of methyl methacrylate oligomer composites

First, 300 g (321 mL) of methyl methacrylate (MMA) was placed in a round-bottomed flask. After adding

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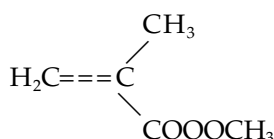
TABLE I
PMMA and PAA Composites^a

PMMA Composites		PAA Composites	
Number	Sample	Number	Sample
1	Virgin PMMA	14	Virgin PAA
2	PMMA-ethanol	15	PAA-ethanol
3	PMMA-isopropyl alcohol	16	PAA-isopropyl alcohol
4	PMMA-butyl alcohol	17	PAA-butyl alcohol
5	PMMA-ethanediol (E _{1,2})	18	PAA-ethanediol (E _{1,2})
6	PMMA-isopropanediol (P _{1,2})	19	PAA-isopropanediol (P _{1,2})
7	PMMA-butanediol (B _{1,2})	20	PAA-butanediol (B _{1,2})
8	PMMA-butanediol (B _{1,3})	21	PAA-butanediol (B _{1,3})
9	PMMA-butanediol (B _{1,4})	22	PAA-butanediol (B _{1,4})
10	PMMA-hexanediol	23	PAA-hexanediol
11	PMMA-hexanol	24	PAA-hexanol
12	PMMA-dodecanediol	25	PAA-dodecanediol
13	PMMA-dodecanol	26	PAA-dodecanol

^a Ethanol: CH₃CH₂OH; E_{1,2}: OHCH₂CH₂OH; B_{1,2}: CH₃CH₂CH(OH)CH₂OH; isopropyl alcohol: CH₃CH₂CH₂OH; P_{1,2}: CH₃CH(OH)CH₂OH; butyl alcohol: CH₃CH₂CH₂CH₂OH; B_{1,4}: HOCH₂CH₂CH₂CH₂OH.

300 mL of chloroform and 1 g of benzoyl peroxide and refluxed gently for 15 min, the polymer solution was divided into several fractions. The first fraction was kept pure without additive. Alcohols or diols, in the same concentration of 3% by weight of the polymer, were added to the remaining fractions to form the PMMA composites.

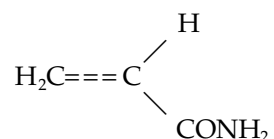
The chemical structure of PMMA monomer is



Preparation of acrylamide oligomer composites

First, 648 g of acrylic acid oligomer was poured in a 1000-mL flask. Next, 540 g of urea was added, and the solution was heated at 140°C for 2 h. The PAA thus formed was divided into fractions. The first fraction was kept pure without additive. Alcohols or diols, in the same concentration of 3% by weight of the polymer, were added to the remaining fractions to form the PAA composites.

The chemical structure of PAA monomer is



The PMMA and PAA composites are described in Table I.

Measurement of the electric conductivity of the polymer

The electric conductivity of thin films of the polymers was measured by a previously described method.⁸ Specimens of 1 cm diameter and 1 mm thickness were tightly adjusted between the plates of two copper electrodes of an electric cell. The electric circuit used was composed of a regulated DC power supply, a high-impedance electrometer (Keithley electrometer of the type 610c), and the cell.

PAL measurements

The PAL measurements were performed in air at room temperature using a fast-fast coincidence system with a lifetime resolution of 230 ps full width at half maximum (fwhm). A 20-μCi ²²Na positron source was deposited on Kapton foil and then sandwiched between two similar pieces of the sample. PAL spectra containing 10⁶–10⁷ counts were collected on each sample. All of the PAL spectra obtained were analyzed with the PATFIT⁹ program, which is a finite term lifetime analysis with τ₁ = 0.125 ns constraint. Continuous lifetime analysis using the LaPlace inversion program CONTIN¹⁰ was employed to obtain the free volume probability density function V_f pdf versus the free volume size V_f, with Al as a reference spectrum.

In lifetime analysis, three lifetime results were obtained. The shortest lifetime (τ₁, I₁) is attributed to positron annihilation from the bulk. The second lifetime components (τ₂, I₂) are attributed to the positron annihilation from the trapped state, with the free electrons at the interface. The longest lifetime (τ₁, I₃) is due to o-Ps annihilation in the free volume.

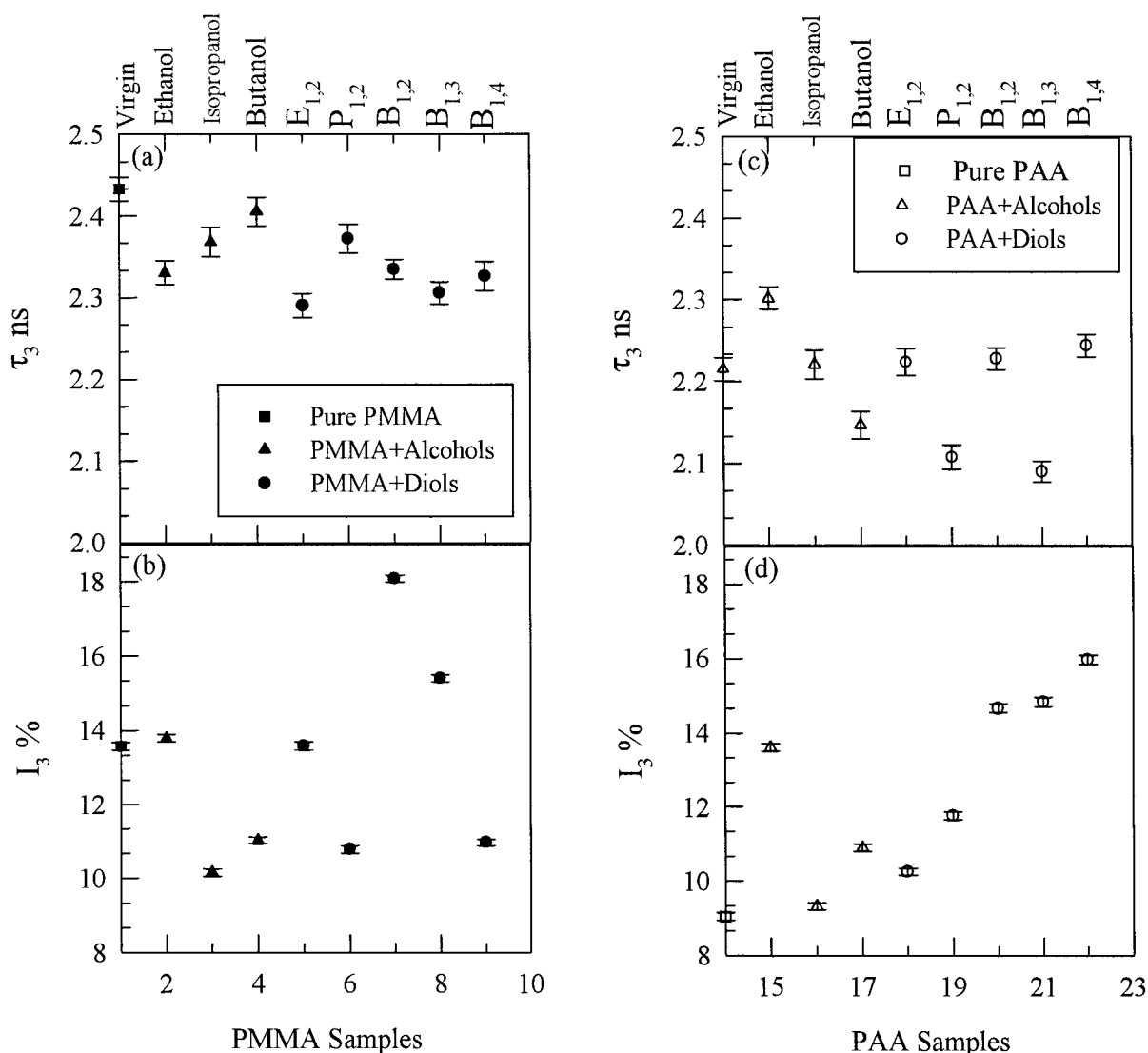


Figure 1 o-Ps lifetime parameters (τ_3 and I_3) versus sample numbers of PMMA and PAA composites.

RESULTS AND DISCUSSION

PAL results

The o-Ps lifetimes (τ_3), which are related to the size of free volume in virgin PMMA and PAA at room temperature, are 2.434 ± 0.026 and 2.215 ± 0.018 ns, respectively. The corresponding intensities (I_3), which are related to the fraction of free volume, are 10 ± 0.09 and $9 \pm 0.09\%$, respectively.

The variations of o-Ps lifetime components τ_3 and I_3 according to the type of polymer composites are shown in Figure 1. The virgin polymers are also included in Figure 1. Because alcohols and diols have hydroxyl (—OH) groups that are capable of forming hydrogen bonds (through the oxygen atom of OH group) with the polymer backbone, it is expected that the higher the number of OH group, the more hydrogen bonds can be formed¹¹. Therefore, the local mobility associated with composites is reduced due to the increase of the crosslinking, which results in the de-

creasing of the free volume size¹². This phenomenon is obvious in all PMMA composites and some of PAA composites (A_{17} , A_{19} , A_{21}), where the o-Ps lifetime τ_3 of the composites is shorter than that of the virgin polymers (see Figs. 1a and 1c). Because of the presence of lone pair electrons on oxygen atoms in PMMA and on nitrogen atoms in PAA polymers, the addition of diols or alcohols increases the electron negativity of the polymer composites. This increase in electron negativity leads to the formation of some regions with high electron density in polymers composites, where the positron can be annihilated within a short lifetime (see Figs. 1a and 1c).

On the other hand, compared with pure PMMA and PAA, the addition of alcohols and diols results in fluctuation of the o-Ps intensity I_3 of PMMA composites and a significant increase in I_3 of PAA composites (see Figs. 1b and 1d). These results are due to the presence of alcohol, which is a good cation scavenger that enhances Ps formation by hole scavenging when

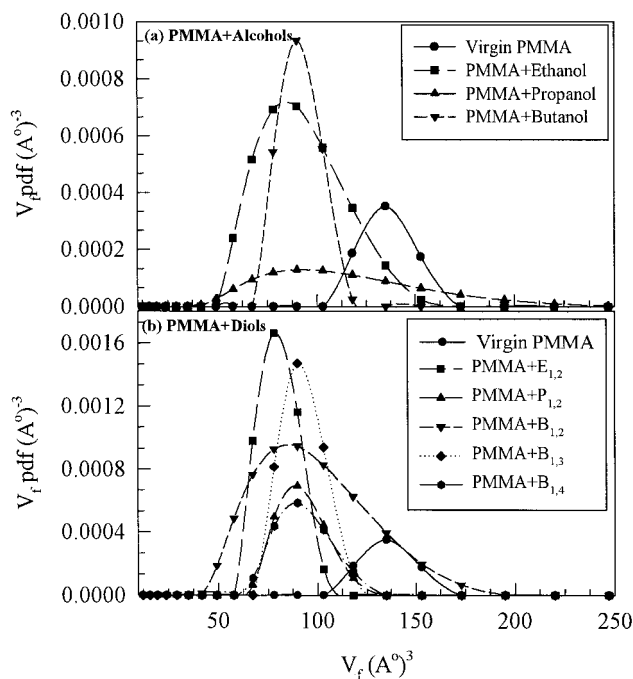


Figure 2 Free volume distributions V_f pdf versus V_f for (a) PMMA-alcohol composites and (b) PMMA-diol composites. Smooth curves are drawn through data points for clarity.

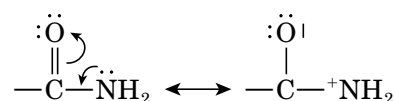
a small amount is added to the polymer.¹³ This reaction can take place because of the higher proton affinity of the alcohol than that of the polymer. Adding molecules with high proton affinity, such as ethanol, isopropyl alcohol, and butyl alcohol, to the PAA polymer increases the hole scavengers and leads to the increase of o-Ps formation, as shown in Fig. 1d.

In PMMA composites, the I_3 values fluctuates above and below that of pure PMMA (Fig. 1b) due to the presence of CH_3 groups, which lead to an equilibrium state for the negative charge region due to a $+I$ inductive effect. In addition, the presence of the high electron negativity of the oxygen atom in the carboxyl group (COOCH_3) increases the secondary bond density between polymer chains and leads to a change in the amount of free volume in the polymer.

The results also show that the values of the o-Ps lifetime components (τ_3 and I_3) depend on the chemical structure of the polymer and the length of the hydrocarbon chain of alcohols or diols in the cases of PMMA- and PAA-alcohol composites and PAA-diol composites. The τ_3 increases and I_3 decrease in the cases of PMMA-alcohol composites, whereas both τ_3 and I_3 decrease in the cases of PAA-alcohol composites with increasing chain length of the alcohol. On the other hand, the I_3 of PAA-diol composites increases according to the number of carbon and hydrogen atoms in the chain. This result indicates that PMMA-alcohol composites contain a free volume with a large size and small fraction, whereas PAA-alcohol com-

posites contain a free volume with a small size and small fraction.

The higher τ_3 and I_3 values for PMMA compared with those for PAA could be interpreted in terms of molecular structure, molecular packing in the polymer, and the substitution effect. The density of crosslinking is high in the PAA polymer, which leads to a small free volume size and a low fraction (i.e., short τ_3 and low value of I_3 , respectively) in this polymer. This result is due to the presence of a high number of hydrogen bonds that result from the high electron density of the oxygen atom, which is due to the resonance effect in PAA:



The free volume distributions obtained for PMMA and PAA composites are shown in Figures 2 and 3, respectively. The sizes of free volume are 139 and 117 \AA^3 for virgin PMMA and PAA, respectively. These results are confirmed by finite lifetime analysis; the average free volume sizes of composites that contain diols are smaller than those that contain alcohols in both PMMA and PAA composites.

Electric conductivity results

The electric conductivity (σ) of PMMA and PAA composites as a function of the sample number (i.e., com-

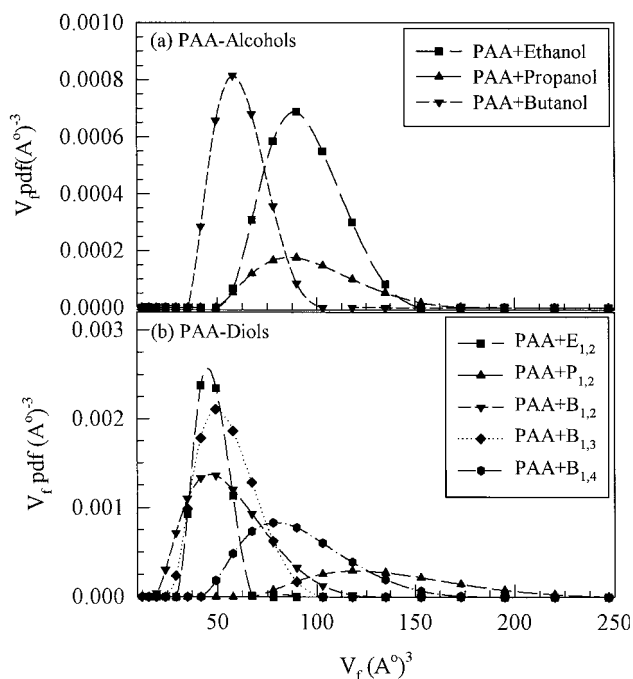


Figure 3 Free volume distributions V_f pdf versus V_f for (a) PAA-alcohol composites and (b) PAA-diol composites. Smooth curves are drawn through data points for clarity.

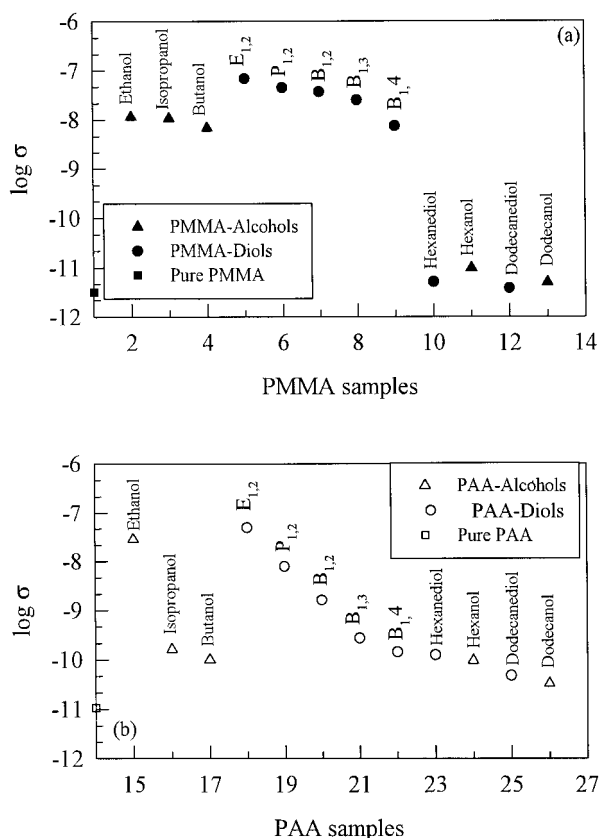


Figure 4 Plot of $\log \sigma$ versus sample numbers of (a) PMMA and (b) PAA composites.

posites) are plotted in Figures 4a and 4b, respectively. The electric conductivity values of virgin PMMA and PAA polymer are 3.16×10^{-12} and 1.07×10^{-11} $\text{ohm}^{-1} \text{cm}^{-1}$, respectively. The higher σ value of pure PAA compared with that for pure PMMA is due to the presence of a polar group (NH_2) in PAA, which increases the electron negativity, compared with the presence of a COOCH_3 group in PMMA, which leads to an equilibrium state for the negative charge region and thereby decreases the conductivity. The σ values for ethanol-polymer (PMMA or PAA) composites are lower than those for ethandiol-polymer composites. The same trend is found for isopropyl alcohol/butyl alcohol-polymer and isopropanediol/butandiol-polymer composites. This result is logical because the presence of two $-\text{OH}$ groups in diols increases the ionization, which leads to an increase in conductivity. The σ value for butanediol ($B_{1,2}$ and $B_{1,3}$)-polymer composites is higher than that for $B_{1,4}$ -polymer composites because of the possibility for condensation between the two $-\text{OH}$ groups in $B_{1,2}$ and $B_{1,3}$. Butyl alcohol-polymer composites have the lowest conductivity.

The electric conductivity was also measured for hexanol-, hexanediol-, dodecanol-, and dodecanediol-polymer composites. When the hydrogen carbon chain is longer, σ is lower, if the number of

carbon atoms in the chain is the same (i.e., hexanol and hexanediol or dodecanol and dodecanediol). Accordingly, the σ value for diol-polymer composites is higher than that for alcohol-polymer composites because of the presence of high numbers of lone pairs of electrons of the oxygen atoms in diols. Therefore, the passing of current will be greater in diols than in alcohols. On the other hand, the conductivity of alcohol- or diol-polymer composites is greater than the conductivity of pure PMMA or PAA. Comparison of PMMA and PAA composites shows that the σ value for PMMA composites is higher than that for PAA composites.

Correlation between lifetime parameters and electric conductivity

Because the intermediate lifetime component is attributed to the annihilation of positrons trapped with free electrons at the polymer matrix-additive interface, the trapping sites might be voids in the amorphous regions of the polymer composites. The intensity I_2 of the intermediate lifetime component is an indicator of

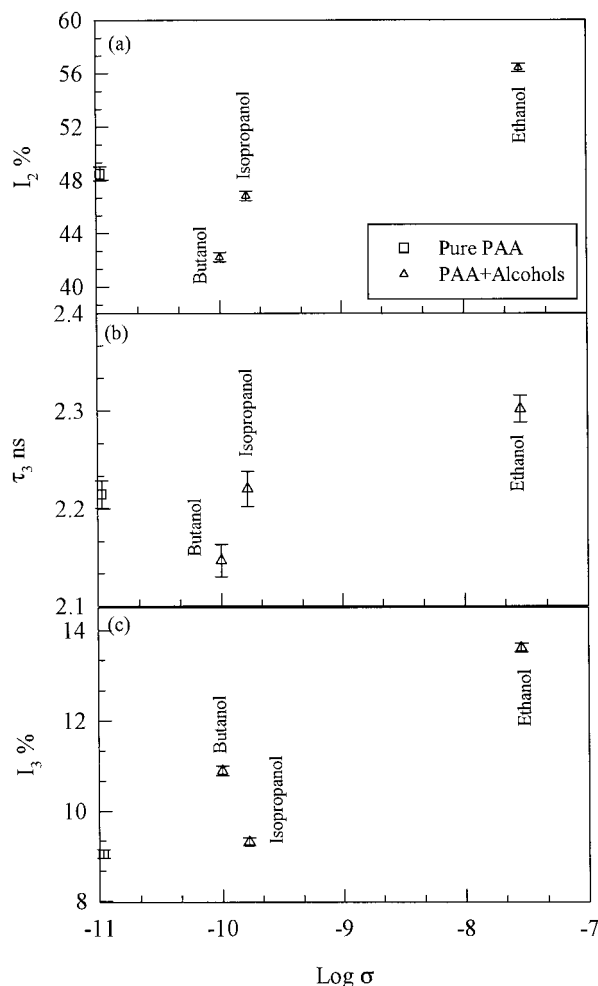


Figure 5 Correlation between $\log \sigma$ and (a) I_2 , (b) τ_3 , and (c) I_3 for PAA-alcohol composites.

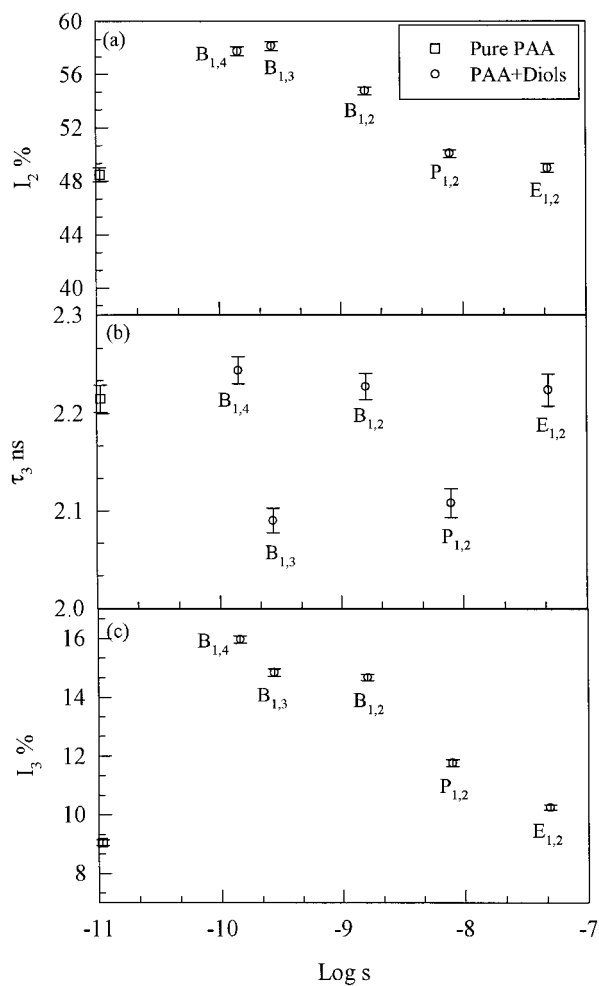


Figure 6 Correlation between $\log \sigma$ and (a) I_2 , (b) τ_3 , and (c) I_3 for PAA–diol composites.

the electric conductivity σ , so the larger the I_2 value, the greater is I_2 .¹⁴

A correlation was found between the lifetime parameters (τ_3 , I_3 , and I_2) and the electric conductivity (σ) of PAA composites (Figures 5 and 6). In PAA composites, the presence of NH_2 group leads to an increase in the negatively charge region and, consequently, an increase in I_2 .

The PAA–alcohol composites exhibit semiconducting properties at large size and high fraction, as shown in Figure 5. On the other hand, PAA–diol composites exhibit semiconducting properties at large size and low fraction, as shown in Figure 6. In the case of PMMA composites, no correlation was found between lifetime parameters and the electric conductivity. These results show that PAA composites are better than PMMA composites for use as conducting materials.

CONCLUSIONS

Measurements of PAL and electric conductivity show that the addition of alcohols and diols to PMMA and PAA results in the formation of good semiconducting materials. The correlation between σ and lifetime parameters show that PAA–alcohol composites exhibit semiconducting properties at large size and high fraction, whereas PAA–diol composites exhibit semiconducting properties at large size and low fraction. Comparison between PAA and PMMA composites following the addition of alcohols and diols shows that the former have better semiconducting properties than the latter. This conclusion was made on the basis of the positive relation between σ and I_2 , because the increase in I_2 is an indicator of the conductivity.

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