Microwave Absorbing Materials Based on Conducting Polymers**

By *Laurent Olmedo*,* *Patrick Hourquebie*, and *Franck Jousse*

Microwave absorbing materials have been based on a combination of compounds in order to generate dielectric and/or magnetic losses. These materials, which have a number of industrial applications, have, however, limitations linked chiefly with constraints of surface mass. Also, the use of dielectric compounds obtained by dispersion of conductive additives (carbon black, graphite, metallic powders) requires the control of both the rate of addition, and the phenomenon of particle aggregation, with an extremely high level of reproducibility. In fact, the function of these materials remains linked to the control of inter-particle electronic transfer. The parameter measured, i.e. (ε', ε'') is thus dependent on the texture of the percolation aggregates and as a result governs the conditions of dispersion.

The object of this article is to show how conductive polymers can supply a solution to this type of problem. From the surface mass point of view, conductive polymers supply solutions with respect to weight reduction, especially in the framework of applications requiring a good compromise between absorption bandwidth and surface mass. Thus, the frequency dependency of (ε', ε'') of several conductive polymers, or the association of these materials with different substrates allows the design of new absorbents. From the reproducibility point of view, the growth methods used during the polymer synthesis lead to materials showing stable property levels compared to materials based on dispersions of conductive particles (in particular carbon black) in an insulating phase.

As only the formulation parameters control the final properties of the material, the chemistry of conductive polymers offers a wide diversity of synthetic methods allowing both the integration of the conductive element in different media (matrix, reinforcement, honeycomb) and the construction of complex structures, giving not only absorption of microwaves but also conforming to environmental constraints. From the point of view of the applications of conductive polymers, several papers have dealt with the production of soluble conducting polymers for making conducting and optically transparent coatings.[1, 2]

Taking account of the conductivity levels of conductive polymers (1 to 50 S/cm) it is necessary to dilute the conductive phase or adjust the doping level to produce an absorbent material whose conductivity ($\sigma = 10^{-3}$ to 10^{-1} S/cm) enables an appropriate surface resistance to be obtained. In addition, these materials often possess poor mechanical properties making them unusable as they are. Also, to define a conductive polymer-based absorbent it is necessary to seek a host material (insulating polymer matrix, porous substrate, textile or fibrous reinforcement) which will confer the following properties on the material:

- A suitable macroscopic conductivity based on dilution of the conductive phase. It would thus be possible to produce an insulating–conductive blend or a composite through deposition on a support.
- Compatibility with classical techniques of polymer (extrusion, injection) or composite production.
- The ability to be mechanically structured when placed on the surface of a composite support such as textile or honeycomb.

The work which we have carried out on polypyrrole, polyaniline, and polyalkylthiophene based absorbents has revealed that polypyrrole is of use because it easily forms blends with insulating polymers; polyaniline has attractive physicochemical properties and has the ability to be deposited onto reinforcing textiles; polyalkylthiophenes exhibit excellent solubility and melting properties, which are usually difficult to get with other conductive polymers.

Polypyrrole: We have shown[5] how percolation boundaries of less than 2% by volume of polypyrrole can be obtained where polypyrrole growth was carried out in situ in an insulating phase (Teflon). The comparison of three materials (dispersion of polypyrrole in rubber or liquid epoxy resin and polypyrrole growth) from the point of view of ε' shows that the advent of high shearing forces with rubber allows the insulation to be preserved up to concentration levels of the order of 40 to 50% by volume. On the other hand, in the case of the epoxide binder, an increase in ε' and dielectric losses appears at low concentrations. However, these properties remain difficult to control. In the case of the blend obtained by in situ chemical growth, we observe a significantly different behavior linked to the extremely low percolation boundary. Such a material shows remarkable properties compared with those obtained by dispersion, particularly due to the non-perturbation of rheological properties of the insulating phase as a result of the low concentration of conductive polymer. In addition, this technique enables the generation of blends with excellent reproducibility of radioelectric properties due to the nature of the growth process itself. Also, this technique has been extended to the production of blends of polypyrrole with conventional thermoplastics. Insulating matrices such as PVC or polycarbonate could be successfully used to obtain devices produced by injection techniques similar to those used for the thermoplastics themselves.

In the case of PVC in particular, a number of synthetic parameters were studied, taking account of the absence of studies since those reported by Myers.[10] Our studies on the effect of the solvent[5] showed that good solvents for PVC (tetrahydrofuran, cyclopentanone) are also Lewis bases compared with the oxidant ($FeCl_3$). Such solvents thus confer to the blend an irregular texture because of the good polypyrrole–PVC interpenetration, but the blends are insulating due to a lack of stoichiometry caused by the reaction of $FeCl_3$

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with solvent. On the other hand, a bad solvent for PVC (nitrobenzene) leads to a nodular structure giving good injectability and high conductivity.

A parallel study was carried out on the effect of hydration of the medium[5] for a blend with 10% by weight of polypyrrole in PVC, to compare the influence on the conductivity of anhydrous ferric chloride, the hexahydrate, and anhydrous $FeCl_3$ with the addition of "free" water in the medium. This showed that the use of ferric chloride hexahydrate completely alters the microstructure of the blend leading to a phase segregation in the form of PVC nodules, similar to those obtained for pure PVC reprecipitated under the same conditions. This can be seen in the SEM micrographs in Figure 1 which show the strong homogeneity of the blends prepared with anhydrous $FeCl_3$, with or without the addition of water (Figs. 1a and 1c). Moreover, a recent study[11] has shown that, as in the case of polyaniline, the imine structure obtained at the time of the polypyrrole synthesis is susceptible to protonation by an acid of HCl type (a by-product of the synthesis). The presence of "free" water in the medium therefore allows the dissociation of the acid, protonation of the chain, and thus explains the increase in conductivity. The effect of "free" water on the conductivity is a 10-fold increase in conductivity.[5] These results clearly show that the nature of the reaction medium directly influences the quality of the blend obtained. We have also studied the influence of the processing technique on radioelectric properties. In order to characterize a polypyrrole/PVC blend at a production temperature of 180 °C, two techniques were used: pressing with a uniaxial pressure of 2000 bar, and injection in a thermoplastic press. Figure 2 shows the radioelectric properties measured between 130 MHz and 20 GHz for both a pressed and injected blend. The pressed material exhibits classical resistive behavior with a variation of ε'' versus frequency, according to a law of the type: $\varepsilon'' \propto K\omega^{-s} = \sigma(\omega)/(\omega\varepsilon_0)$ as previously observed,[5] where, K = constant, ω = angular frequency (rad/s), and σ = conductivity (S/cm).

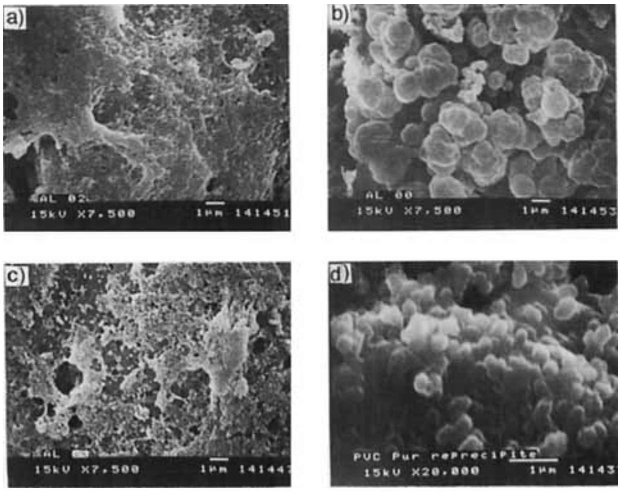

Fig. 1. SEM photographs of polypyrrole–PVC composites synthesized with different types of $FeCl_3$: a) anhydrous $FeCl_3$. b) $FeCl_3 \cdot (6H_2O)$; c) anhydrous $FeCl_3$ plus 6 moles of added free water; d) pure reprecipitated PVC.

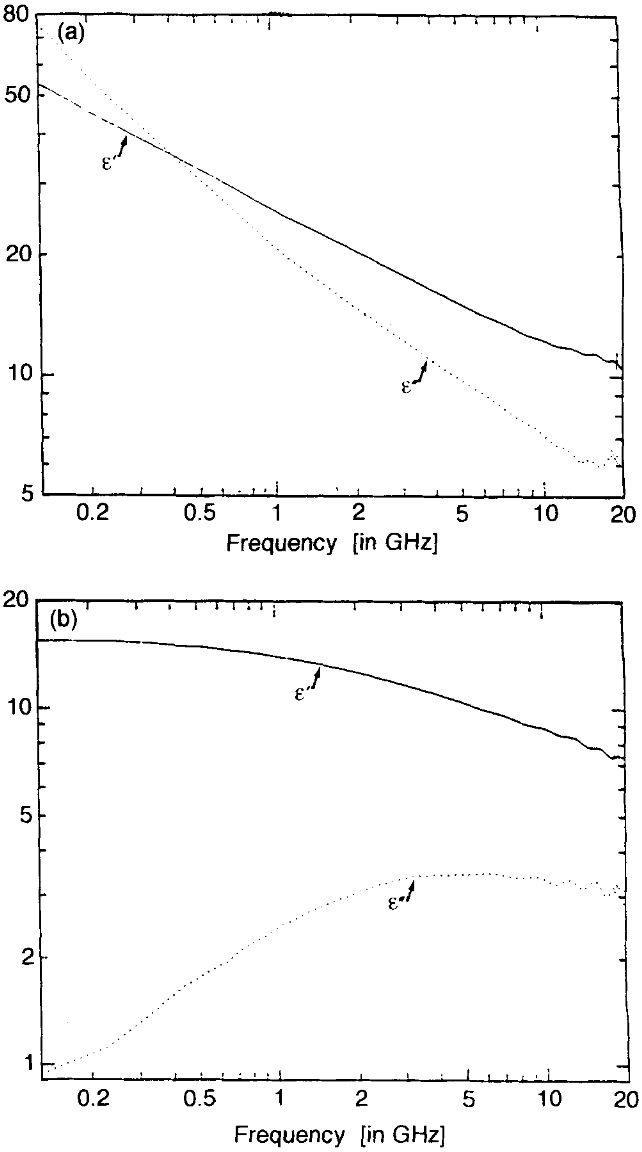

Fig. 2. Variation of (ε',ε'') for a pressed polypyrrole–PVC blend (a), and for an injected polypyrrole–PVC blend (b).

In contrast, injection leads to a material for which ε' decreases slightly at high frequency (modification of blend during injection) and which towards 5 GHz shows a dielectric relaxation explainable by a modification of the blend microstructure in which the aggregates formed during growth are individualized (coating and reduction of grain size) at the time of the injection phase, thus giving rise to a Maxwell–Wagner type relaxation at high frequency. Indeed, the material obtained after production is macroscopically insulating, and may thus be linked to a dispersion of conductive inclu-

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sions (polypyrrole) in an insulating matrix (PVC). The relaxation frequency expression[12] is thus: $f_r = \sigma_2/[2\pi\varepsilon_0(2\varepsilon'_1 + \varepsilon'_2)]$, where ε_0 is the permittivity in vacuo, σ_2 is the conductivity of the conductive inclusion, ε'_1 and ε'_2 corrspond to the real permittivities of the matrix and the conductive material respectively. From this simple expression, it follows that the relaxation frequency (of Maxwell–Wagner type) is a direct function of the conductivity and can thus vary over a wide range. A calculation with $\sigma_2 = 1\ \mathrm{S\,cm^{-1}}$, $\varepsilon'_1 = 4$, and $\varepsilon'_2 = 300$ gives $f_2 = 5.8$ GHz. Similar phenomena have also been observed for the charged polymers TTF–TCNQ[13] and for polyaniline.[14]

The difference in observed behavior (Fig. 2) affects the determination of the coefficient of reflection. The pressed material is difficult to tune in a monolayer, while the injected material (Fig. 3) is resonant and has a wide peak leading to a high level of performances over a wide frequency range.

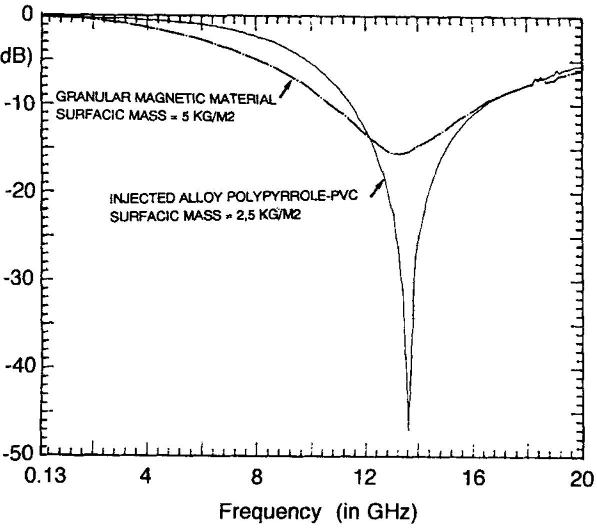

Fig. 3. Comparative reflection properties for an injected polypyrrole–PVC blend and a magnetic granular material.

For comparison, Figure 3 shows the reflection coefficient measured on a 2 mm thick polypyrrole/PVC blend and a granular magnetic material (dispersion of iron carbonyl powder in an elastomer) tuned to the same frequency. Bandwidths of the same order of magnitude were obtained, the surface mass being 2.6 kg/m^2 for the blend compared with 5 kg/m^2 for the granular magnetic material.

Polyaniline: The important characteristic of polyaniline is a reversible variation of conductivity and of ε^* with the doping level, directly related to the pH of the doping solution. For example, reversible variation of ε^* with the doping level can be obtained electrochemically. This variation is an important property in order to get tunable absorbing materials. Such behavior is observed in the case of polyaniline-coated fibrous substrates. The control of synthesis conditions give rise to very homogenous layers (around 100 nm thick) of conducting polymers leading to well controlled properties.

The microwave properties of manufactured composites are completely specific and enable production of materials possessing a very large bandwidth. The broad range of conductivities obtained in this case allows very efficient absorbing design such as gradient stacking. For example, passbands of −10 dB between 5 and 20 GHz have been produced for an increase in surface mass from 4 to 5 kg/m^2 with respect to the composite material, while a traditional non-structural absorbant would need double the surface mass.

Poly(3-octylthiophene): This material exhibits interesting properties in the hyperfrequency area (Fig. 4) particularly in the control of low levels of ε''. Evaporation speed controls the microstructure and the nature of the radioelectrical properties of the blend. For example, Figure 4 shows the differences between a slowly evaporated blend (Fig. 4a: duration 16 hours) and a rapidly evaporated blend (Fig. 4b: duration 10 minutes). In the first case, the appearance of a phase separation (light nodules = insulating phase) creates a medium of very low conductivity ($\sigma < 10^{-9}$ S/cm) where the level of ε' is essentially due to the interfacial polarization. In contrast, in the second case, the material is totally homogeneous on the micrometer scale with a macroscopic conductivity ($\sigma = 5 \times 10^{-3}$ S/cm) leading to classical conductor radioelectric behavior. These observations demonstrate firstly the possibilities of this type of blend. Secondly the variation of ε', ε'', in the case of Figure 4a (typically $\varepsilon_{4\,\mathrm{GHz}} = 10 - j\,3$ $j = \sqrt{-1}$. These levels of (ε', ε'') and ($\varepsilon' > \varepsilon''$) lead to tunable absorbing materials with strong absorption peaks) enables the production of absorbents tuned to −20 dB regardless of the thickness used (Fig. 5b). This property is extremely interesting and is impossible to obtain with a traditional granular material or pure conducting polymer. As can be seen in Figure 5a, this property is impossible to get with poly(3-octylthiophene) alone. In this case, changing the thickness quickly leads to absorbents with lower efficiencies (≥ -20 dB).

In conclusion, the development of conductive polymers applied to microwave absorption has led to the emergence of some extremely novel applications. Going from laboratory to pilot scale still remains a key step for the production of structures intended for attenuation measurements in an anechoic chamber, a necessary condition for any verification of a concept and the realization of practical objectives. This necessity has allowed the development of materials for which there is reasonable hope of industrial applications in the medium term.

In parallel, this work can only progress efficiently if the phenomena encountered are understood. It is for this reason that considerable effort is being expended both in modeling and in the synthesis of model materials. In particular, the orientation of macromolecular chains and the production of soluble conductive polymers of controlled chain length constitute the main lines of research with a view to a better

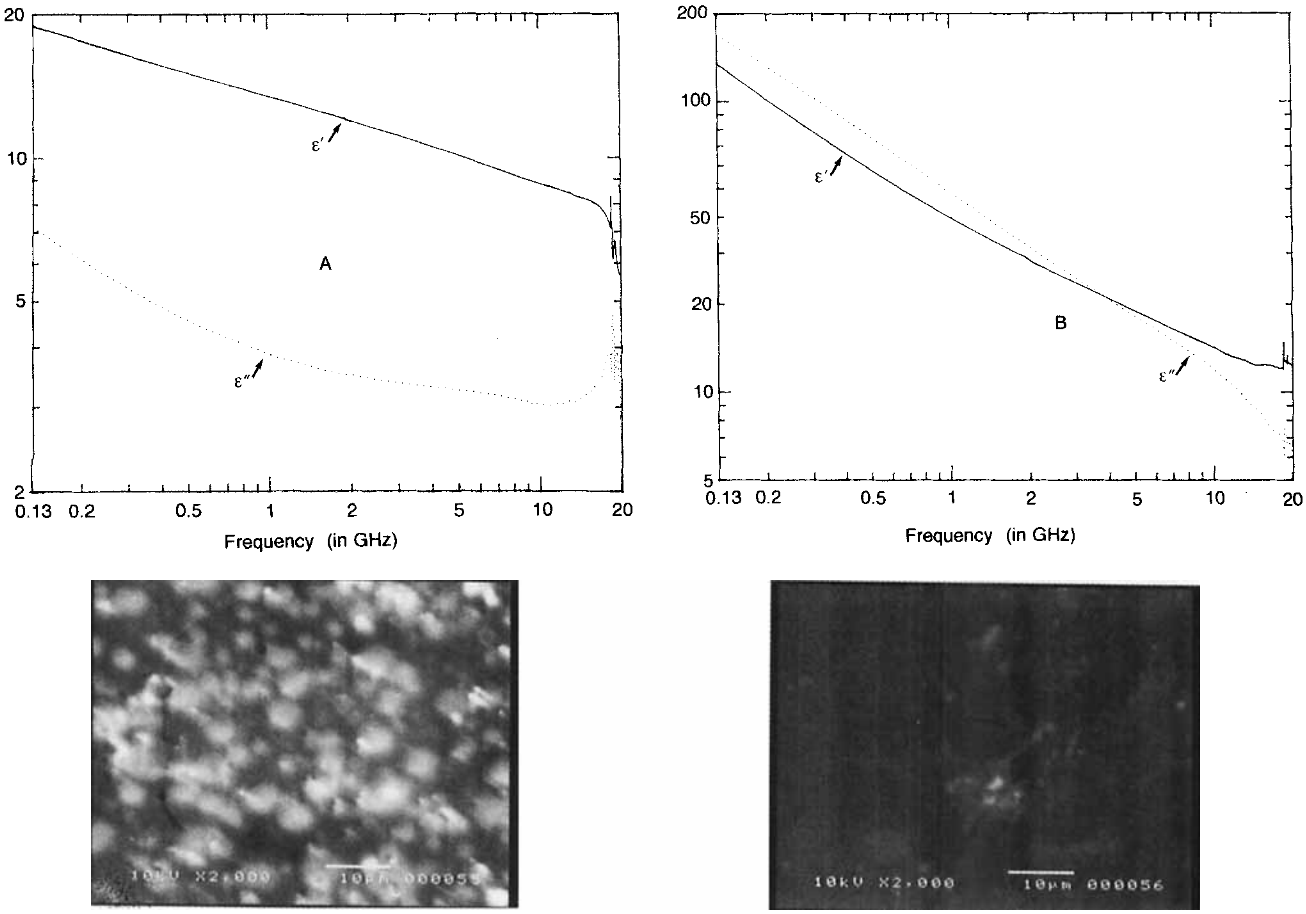

Fig. 4. Variation of the radioelectric properties (ε', ε'') for a polyoctylthiophene EVA blend (30% by weight) for two evaporation conditions: a) slow evaporation; b) rapid evaporation.

understanding of the conduction properties of conductive polymers in the hyperfrequency area.

Experimental

Polypyrrole: The variety of synthetic methods described in the literature for polypyrrole has led us to investigate methods of obtaining conductive polymer–insulating polymer blends which are capable of being processed. We have thus been led to develop several techniques for synthesizing polypyrrole-based blends with a view to producing materials of controlled conductivity, and have developed a) an electrochemical synthetic technique of polypyrrole–elastomer blends, giving films easily assembled by co-vulcanization [3], b) a vapor-phase synthetic technique for polypyrrole intended to achieve the impregnation, in the form of conductivity gradients, of porous substrates (foams, honeycombs) [4], c) a synthetic technique for polypyrrole-thermoplastic blends in powder form [5].

For example, the work carried out by Bjorklünd [6] led us to develop a specific synthetic method based on the last technique. In parallel, comparative experiments have been carried out on granular materials obtained by dispersion of conductive polymer in powder form in an elastomer or epoxy resin [5].

Some blends were synthesized by in situ growth of polypyrrole in a solution of insulating polymer (PVC, polycarbonate, polyphenylene oxide...) or an emulsion of insulating polymer (PTFE) according to the technique of oxidative coupling by $FeCl_3$ [6]. The implementation was then carried out by cold isostatic pressure (3000 bar) in the case of polypyrrole–Teflon or by injection press in the case of the polypyrrole–thermoplastic systems. In addition, dispersions of polypyrrole powder in an elastomer or an epoxy resin were produced. The elastomer-based formulation was produced in a cylindrical mixer, then vulcanized. Experimental details are given in [5]. The epoxy-resin-based formulation was obtained by dispersion of the powder with a turbine. The mixture was degassed under vacuum, then cross-linked at room temperature.

Polyaniline: In comparison with polypyrrole, which as we have just observed is of considerable interest from the technological viewpoint, polyaniline presents extremely special characteristics, making this polymer a promising candidate for phenomenological studies on dielectric behavior towards microwaves, i.e.: the dendritic nature of the polymer, in contrast to the nodular structure observed for polypyrrole; reversible variation of conductivity and ε^* with the pH of the dopant solution; diversity of possible technological applications such as deposition onto fibers [7], or grafting of reactive groups enabling synthesis of polyaniline-polyimide blends [1], or specific variation of the radioelectric properties with frequency according to the method of preparation or the degree of anisotropy of the material.

Emeraldine salt powder was synthesized by the oxidation of aniline monomers using ammonium peroxydisulfate in a 1 M HCl solution while the temperature was kept at 0 °C. The powder obtained was washed with water, then with a dilute NH_3 solution and again with water in order to obtain emeraldine base powder. This powder was then doped using HCl solutions with various pH.

With respect to the production of structural and absorbent materials, polyaniline presents several advantages, in particular its ability to be deposited in thin layers on fibrous substrates. The advantage in such a technique is the possibility of rendering an initially insulating textile conductive. However, in addition to this special feature, it is above all possible to fine tune the surface conductivity of the textile by the synthesis conditions, and thus have access to a wide range of conductivities (10^{-5} to 1 S/cm). The only existing conductive textile being carbon-fiber based (which acts as a reflector to microwaves), such a process is of obvious interest in that it combines structure (formed by the textile) with conductivity. There have been reports of the deposition of polypyrrole onto textiles [8] and polyaniline onto glass substrates [9].

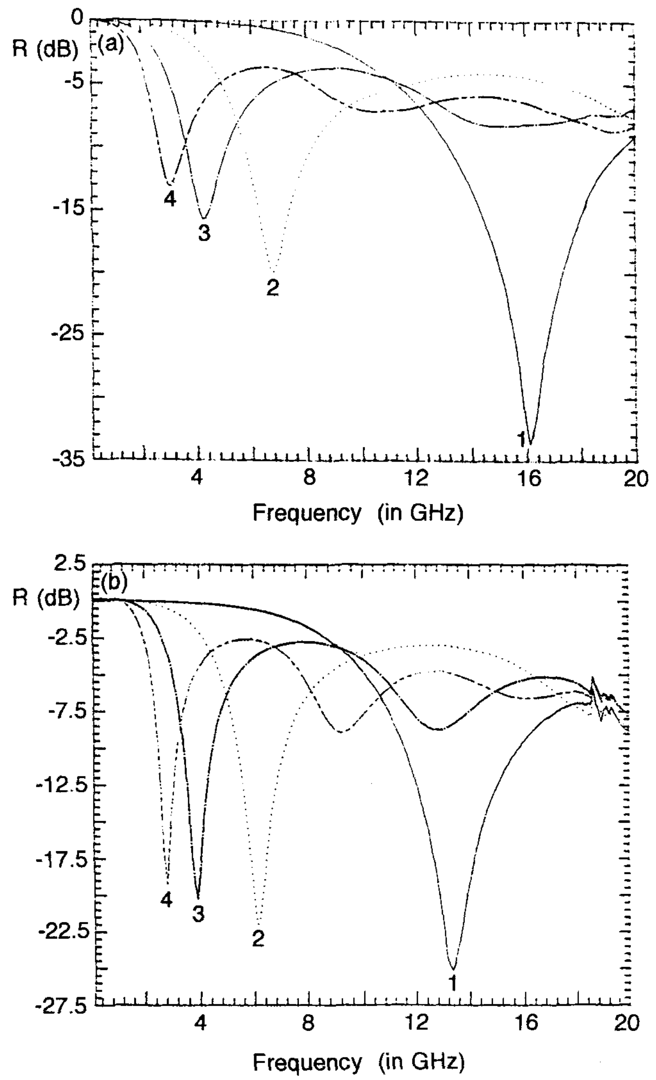

Fig. 5. Variation of the coefficient of reflection with frequency for different thicknesses e of: a) poly(octyl-3-thiophene), (doping level [Fe/S] = 0.064). b) polyoctylthiophene–EVA blend (30% by weight). 1: e = 2 mm. 2: e = 4 mm. 3: e = 6 mm. 4: e = 8 mm.

We have studied two ways of synthesis which are: a) a one step process: the substrate is dipped into a solution containing monomer (aniline or pyrrole), oxidizing agent [$(NH_4)_2S_2O_8$], $FeCl_3$... and the doping agent (sulfonated compound: p-toluene sulfonic acid...). b) a two step process: the substrate is first dipped into the monomer solution and then in the oxidizing agent solution containing the doping agent. This technique can lead to the development of a continuous process due to short reaction times. In both cases the layer thickness is of the order of 100 nm, and conductivities obtained range from 10^{-5} to 1 S/cm.

Polyalkylthiophenes: The polyalkylthiophenes show promising physicochemical properties which allow the production of conductive polymer–insulating polymer blends. These properties are, firstly, their solubility in the reduced state in solvents such as chloroform and THF, and secondly the existence of a melting point in the case of polyoctylthiophene.

The "molten" polymer can thus be mixed with an insulating polymer to obtain a blend, which, after doping, becomes conductive. We have chosen to study poly(3-octylthiophene) which has a good combination of high conductivity level and good solubility. Poly(3-octylthiophene) was synthesized by oxidation of 3-octylthiophene using iron(III) chloride in chloroform. The powder obtained is washed using methanol and acetone in order to remove iron(III) chloride used in the synthesis. The material obtained becomes conductive after doping in a solution of iron(III) chloride in nitromethane. It is then easy to get any conductivity in the range 10^{-9}–10 S/cm by changing the doping time and the concentration of the solution used in the doping procedure.

A solution of a conducting polymer containing a traditional thermoplastic (PVC, polystyrene, EVA) can also be evaporated to give films with good mechanical characteristics.

Poly(3-octylthiophene) powder was dissolved in THF. Various amounts of EVA (ethylene–vinyl acetate copolymer) were then added. The solution thus obtained is poured onto a glass substrate and slowly evaporated. Various films containing different amounts of poly(3-octylthiophene) were obtained. The films were doped using the procedure previously described for poly(3-octylthiophene) powder. It is then possible to get the desired conductivity by varying the doping level and the poly(3-octylthiophene) content.

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$(Me_5C_5)SiH_3$ and $(Me_5C_5)_2SiH_2$ as Precursors for Low-Temperature Remote Plasma-Enhanced CVD of Thin Si_3N_4 and SiO_2 Films

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Silicon oxide and silicon nitride films are of great interest because they have found many applications in fields such as microelectronics, materials science, and optics. Present standard processes for the chemical vapor deposition (CVD) of SiO_2 and Si_3N_4 films are carried out predominantly using silane, SiH_4.[1] Due to its high reactivity and problematic handling there is a demand for non-hazardous alternatives. Substituting one or more hydrogen atoms of silane by organic groups should lead to tailored compounds which meet desired requirements (for example, enhanced stability but still sufficient volatility). In this communication, we report results from remote plasma-enhanced chemical vapor deposition (R-PECVD) studies using the pentamethylcyclopentadienyl-substituted (Cp*-substituted) silanes Cp*SiH_3 and

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