to produce a strong tough polymer which can rapidly retract to its original dimensions on heating above the PSt T_g. Potentially such ABCPs could be used as heat shrink materials if fabricated into some appropriate shape and subsequently deformed to larger dimensions at elevated temperature.

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Dilatometric studies on PVC-Cu composite

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Impregnation of metallic fillers in the polymer matrix enhances the strength and electrical conductivity of the resulting metal-polymer composite[1-8]. In a previous paper[6] we have shown that better coalescence of the matrix markedly enhances the strength and electrical conductivity of poly(vinylchloride)-copper (PVC-Cu) composites. However, no systematic investigation has so far been made to explain the nature of interaction between the phases. Unlike fibre reinforced composites for which the strength of the interfacial adhesion is normally determined by the single fibre pull out experiment, there is no direct method in the particulate composites to measure the magnitude of the strength of the interfacial bonding and mechanism of failure under applied stress. In the present investigation, an attempt has been made to understand the strengthening mechanism through dilatometric studies of PVC-Cu composites.

Commercially available poly(vinylchloride) powder (NOCIL, Bombay) of average particle size 126 μm and copper powder (Assam Carbon Company) of average size 7 μm were used here. Details of the preparation of PVC-Cu composites has been given elsewhere[4,5].

Glass transition temperature (t_g) was measured using a quartz dilatometer. The rate of heating was 1°C min^{-1}. The range of temperature studied was 32-100°C.

Figure 1 shows that glass transition temperature of pure PVC is increased from 85° to 88°C for 5 volume % and to 90°C for 10 volume % metal concentration. Beyond 10 volume % t_g is hardly affected. This is presumably because of the complete formation of segregated network around 10 volume % beyond which increase in metal content does not improve the metal-metal contact condition significantly[5,9,10]. Similar observations have been made by a number of authors in this field[11-16]. Increase in t_g proves segmental immobilization of the pure

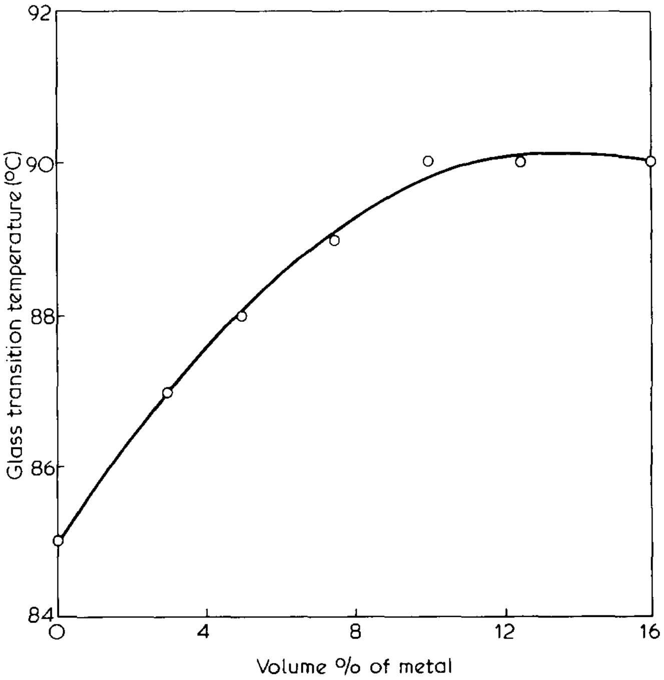

Figure 1 Glass transition temperature of PVC—Cu composite as a function of metal concentration

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polymer by the incorporation of metal. Shift in t_g also points to strong adhesion between the phases. Recently Aras, Sheldon and Lai[17] observed an increase in t_g of poly(vinylacetate) due to the impregnation of silica filler. They ascribed this increase due to the adhesion between the filler and the polymer.

In conclusion, dilatometric studies indicate the existence of a physical adhesion factor between the polymer and metal phases which causes segmental immobilization of the polymer. This may be responsible for the strengthening of the polymer matrix in the composite. Thermal analyses (d.t.a., d.t.g. and t.g.) have been taken up with a view to understanding the exact nature of the interaction between the matrix and the filler phases.

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Ion pair dissociation equilibria for iodonium and sulphonium salts useful in photoinitiated cationic polymerization

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During the past ten years, photochemically initiated curing of surface coatings has grown in importance and may be accomplished by both free radical (essentially acrylic systems) and cationic (essentially epoxide systems) processes[1].

Photochemically initiated cationic curing of epoxy systems involves photodecomposition of various aryl diazonium[2], diaryl iodonium[3], and triaryl sulphonium[4] salts having relatively stable non-nucleophilic anions such as PF_6^-, SbF_6^-, BF_4^-, etc. A notable feature of such photochemically-initiated polymerizations is the apparent effect of the anion on the extent and rate of epoxide consumption[3-5].

Pappas has shown[6] that iodonium salts and sulphonium salts exhibit different activities in the presence of various photosensitizers and rather similar differences are observed in rates of decomposition of the same salts when promoted by reducing organic radicals[7].

For any process occurring via charged species it is necessary to consider potential additional complications arising from ion pair dissociation equilibria[8], viz:

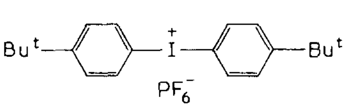
$$[\text{cation}][\text{anion}] \overset{K_D}{\rule[0.5ex]{3em}{0.4pt}} [\text{cation}] + [\text{anion}]$$

Except in special circumstances it is to be expected that free ions will be more reactive than ion pairs, although the influence of ion pairing on the precise mechanistic pathways for reactions of a photochemical excited ion is not easy to predict.

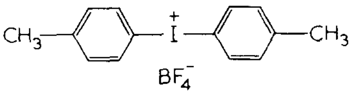
In earlier work[9-11] we have been concerned with the determination of ion pair equilibria and reactivities for salts or relatively stable organic cations and considered it useful, therefore, to attempt similar characterization for the initiating components of important cationic photocure systems.

Experimental details for the techniques of conductance measurement and solvent purification have been fully described in previous papers[9,10]. Analytical data for the salts investigated (I–III) are given in *Table 1*.

Values of K_D, λ_0, ΔH_0, and ΔS_0 for the salts I–III are equivalent conductance on salt concentrations in the solvents CH_2Cl_2 and CH_3CN by the method of Fuoss, with computerized iteration as previously described[9,11].



(I)



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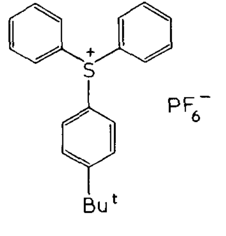

(III)

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