

Thermal Modification of Poly(vinyl Chloride) and Formation of Dehydrochlorinated Poly(vinyl Chloride)–Poly(methyl Methacrylate) Polymer Blend in the Process of Foaming: Identification and Application*

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Synopsis

Impact resistant plastic foam of dehydrochlorinated poly(vinyl chloride) (DHPVC)—poly(methyl methacrylate) (PMMA) was prepared for cryogenic insulation in space vehicle by the method of compression molding and chemical blowing. Impact resistance was achieved by the formation of the polymer blend, dehydrochlorinated poly(vinyl chloride)–poly(methyl methacrylate), during the process of foaming the mold at the temperature of 200°C. The polymer blend was separated from the plastic foam and the compatibility was investigated by ultraviolet, infrared spectral studies and differential scanning calorimetry (DSC). The compatibility of dehydrochlorinated poly(vinyl chloride) and poly(methyl methacrylate) was highlighted on the basis of allylic activation introduced in the thermally modified poly(vinyl chloride). The thermodynamic views were also correlated. The versatility of the present method for impact-resistant foam was pointed out.

INTRODUCTION

Impact resistant plastic foams are useful in the application of thermal and cryogenic insulation. The impact resistance is gained by polymer blending and high impact strength is obtained when there is optimum compatibility between the plastic and the rubbery phase.¹ Several methods such as mechanical blending, block copolymerization, graft copolymerization, and interpenetration of two networks have already been established for polymer blending, and all the methods of preparing impact resistant plastic foams utilized the polymer blend as starting material.^{2–4} The present method highlights the preparation of the impact-resistant plastic foam from the homopolymers of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA). Thermal modification of poly(vinyl chloride) and compatibility between the dehydrochlorinated poly(vinyl chloride) and poly(methyl methacrylate) were simultaneously effected at the foaming temperature of the mold (200°C). The aim of the present work was to explore the possibility of simultaneous blending and foaming to get impact-resistant plastic foams.

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EXPERIMENTAL

Raw Materials

For the optimum performance as insulating material, the following formula was adopted to prepare a rigid, impact resistant plastic foam:

PVC resin (Jai Enterprises, Madras, India)		100 parts by wt
tri(cresyl phosphate) (TCP)	plasticizer	27.5 parts by wt
PMMA (Transoptic powder No. 20-3400 A, Buehler Ltd., USA)		27.5 parts by wt
barium-cadmium and magnesium stearate	stabilizer	10.0 parts by wt
palmitic acid	surfactant	1.0 parts by wt
aluminium chloride	curing agent	2.0 parts by wt
paraffin wax	blowing agent	5.5 parts by wt
calcium carbonate		17.0 parts by wt
cyanuric chloride		4.5 parts by wt

Preparation of Molding Compound

The molding compound was prepared by mixing as per the order of the formula.

PVC resin (powder form) was preheated at the temperature of 60°C for 5 min to drive off surface moisture and to condition the resin particle for fast absorption of plasticizer.⁵ Then tri(cresyl phosphate) was added and thermally treated at the temperature of 80°C for 0.5 h until the whole mass dried. PMMA (transoptic powder) was then added, and the whole mixture was transferred to the laboratory type ball mill and mixed for 10 min (100 rpm). All other ingredients were added subsequently, and the whole mixing in the ball mill was done for not more than 45 min.

Molding

The molding compound was transferred into a cylindrical mold and compression molded. Molding conditions were 120°C at 4000 psi (2.8×10^7 Pa) for 15 min, cooling to 60°C within approximately 5 min. The specimen Mount Press, Buehler Ltd., U.S.A., was used for this purpose (Fig. 1).

Foaming

The mold was then supported in a paper cylinder of 2.5 cm diameter and subjected to foam in a circulating-air oven. Foaming conditions were 200°C for 1 h and air cooling. The purpose of circulating-air oven was to avoid the autocatalytic activity of hydrochloric acid (which was eliminated at the temperature

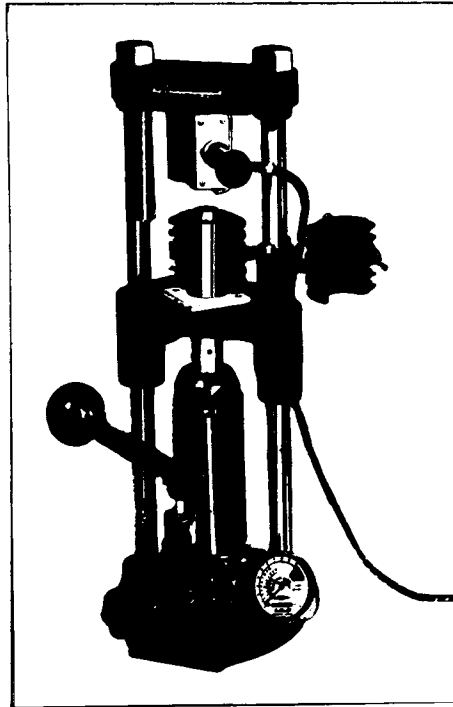


Fig. 1. Specimen mount press.

of 200°C) in the dehydrochlorination of poly(vinyl chloride).⁶ The aim here was only to preserve lesser degree of dehydrochlorination. The foaming action was effected in the softened mass by gas generation as reported by Ghatge and Phadke.⁷

Izod Impact Test

The foam was subjected to the Izod impact test.⁸ The Avery Izod Impact Testing Machine with the striking velocity of 2.44 m/s was used. The impact strength for the present foam (notched specimen of 1 cm² cross-sectional area) was found to be 4 kgf/cm. For the comparison of the impact strength, a PMMA foam was prepared using the composition mentioned earlier excluding PVC and TCP.

Molding conditions were 120°C at 4000 psi (2.8×10^7 Pa) for 5 min and cooling to 60°C within approximately 5 min. Foaming conditions were 220°C for two hours in the air oven and air cooling. The impact strength for PMMA foam was found to be 2.75 kgf/cm. An increase in impact strength was achieved when PMMA was mixed with PVC. This increase would only be due to the polymer blend which could have formed during the process of foaming.

In order to investigate for the polymer blend, the foam (prepared from PVC, PMMA mix) was subjected to separation analysis.

Separation Analysis

The finely ground sample (1–2 g) of the foam was subjected to ether and methanol extraction using the Soxhlet extractor, subsequently, to remove the plasticizer and stabilizer, respectively. The polymer blend was then separated from the deplasticized sample as described by Harsaw et al.⁹ Care was taken to avoid degradation due to mastication.¹⁰ Then the recovered polymer blend was dried in vacuum at a temperature of 60°C and stored for analysis.

Analysis of the Blend

A polymer blend of 1.0% concentration in dimethylformamide was prepared and subjected to UV spectral analysis. The Specord UV-VIS, Carl-Zeis Jena DDR instrument was used. Thin film of polymer blend of DHPVC—PMMA cast from tetrahydrofuran was subjected to IR spectral analysis. The Perkin-Elmer 337, Grating IR Spectro Photometer was used. The Perkin-Elmer DSC 1B model was used for thermal analysis. The sample was first heated at the rate of 16°C/min above 200°C and subsequently cooled at low temperature (30°C). The T_g value was recorded after the second heating run at the rate of 16°C/min.

RESULTS AND DISCUSSION

UV Spectral Analysis

Qualitative and quantitative determinations of thermal modification in polymer were done by UV spectral analysis. A broad absorption band at the wavelength region of 265.7 $m\mu$ was observed with the absorbance of 0.64. This was due to some modification occurred in the polymer. Care was taken to know which polymer (either PVC or PMMA) underwent thermal modification. It had been expected that either PVC or both PVC and PMMA would have undergone modification (modification in PMMA would be due to the abstraction of HCl from PVC). Therefore, the PMMA foam, prepared for the purpose of the Izod impact test was subjected to IR spectral studies and no qualitative indication for modification was observed (Fig. 2). PMMA was also thermally stable at the temperature of 220°C without any chain scission,¹¹ retaining its original spectral features. Therefore, the modification was nothing but unsaturation in PVC due to the dehydrochlorination during foaming.

A standard UV spectra of $H(CH=CH)_nH$ model compound was used for comparison.¹² It was assumed that the band at 265.7 $m\mu$ for polymer blend would correspond to approximately three conjugated double bonds in a sequence of a chain. This was further verified using the Lewis–Calvin equation

$$\lambda^2 = Kn$$

where K 22,400 $m\mu^2$ (calculated as per the assumption that the curve $\lambda^2 - n$ is approximately a straight line for a small range of n ,¹³ e.g., $2 \leq n \leq 3$). Number of monomer with double bond present in 100 monomer = 3.0 monomer (average number of monomer units in a chain¹⁴ of PVC = 100). Degree of polymerization of PVC = 1108, determined from molecular weight (\bar{M}_v) therefore, number of monomer with double bond present in 1108 monomer = $1108 \times 3.0/100 = 33.24$

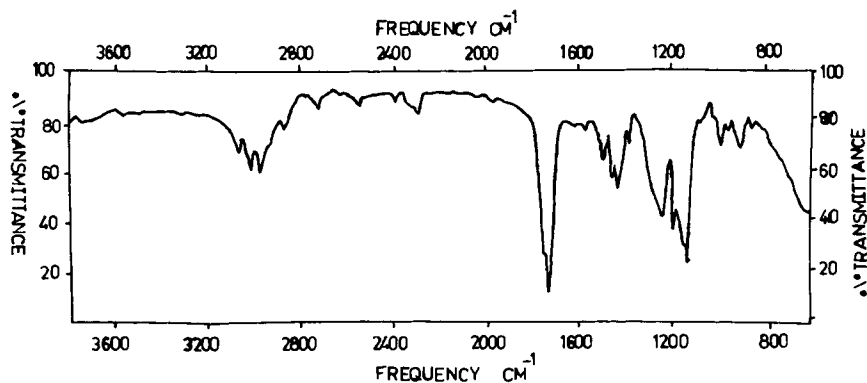


Fig. 2. IR spectra of PMMA.

= 33 monomers. Percentage of monomer with double bond present in DHPVC
 = $33.24 \times 100/1108 = 3\%$

From the percentage of the dehydrochlorinated monomer unit it was concluded that the physical properties of PVC would not have changed appreciably but would have created active methylene group sites which would have played an important role in mixing of polymers.

IR Spectral Analysis

Mixing (compatibility) of DHPVC and PMMA was further investigated and identified from the IR spectra (Fig. 3). The observed changes were mentioned in the Table I.

Differential Scanning Calorimetry

The glass transition temperatures were determined as the temperature corresponding to one-half the increase in heat capacity at the transition. The DSC scan for the polymer blend in Figure 4 showed three transition regions with the T_g at 69.5°C, 83°C, and 100.5°C. The low T_g was probably due to the breakdown

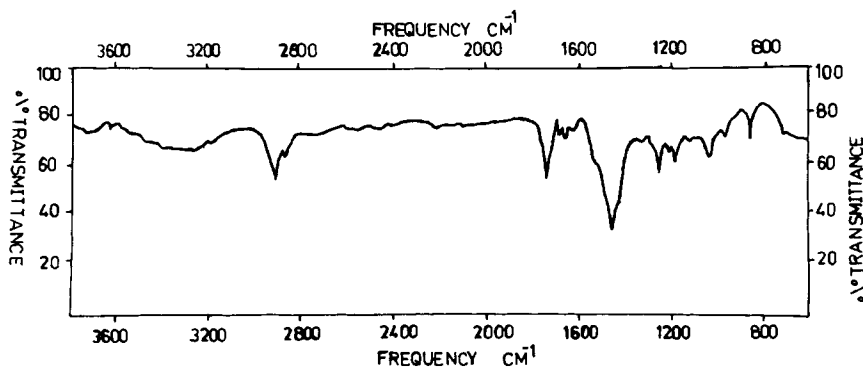


Fig. 3. IR spectra of DHPVC—PMMA blend.

TABLE I
Observed Changes in IR Spectra of DHPVC—PMMA Blend

Frequency (cm ⁻¹)	Change	Probable assignment
1149	sharp peak	ester —C—O group
1250	sharp peak	=CH bending
1414–1431	sharp peak	—CH ₂ bending
1610	sharp peak	conjugated double bond
1640–1680	feeble peak	unconjugated double bond
1740	sharp peak	ester group —C=O
3400	broad peak	—OH stretching (intermolecular H ₂ bonding)

of the intermolecular crosslinks (of low dissociation energy) between DHPVC and PMMA. The T_g at 83°C and 100.5°C was probably due to transition behavior of broken DHPVC and PMMA fragments, respectively. In the second scan a single broad transition region (340–385°K) appeared. The T_g which appeared at 69.5°C in the first scan was so diffuse in the second scan as to go

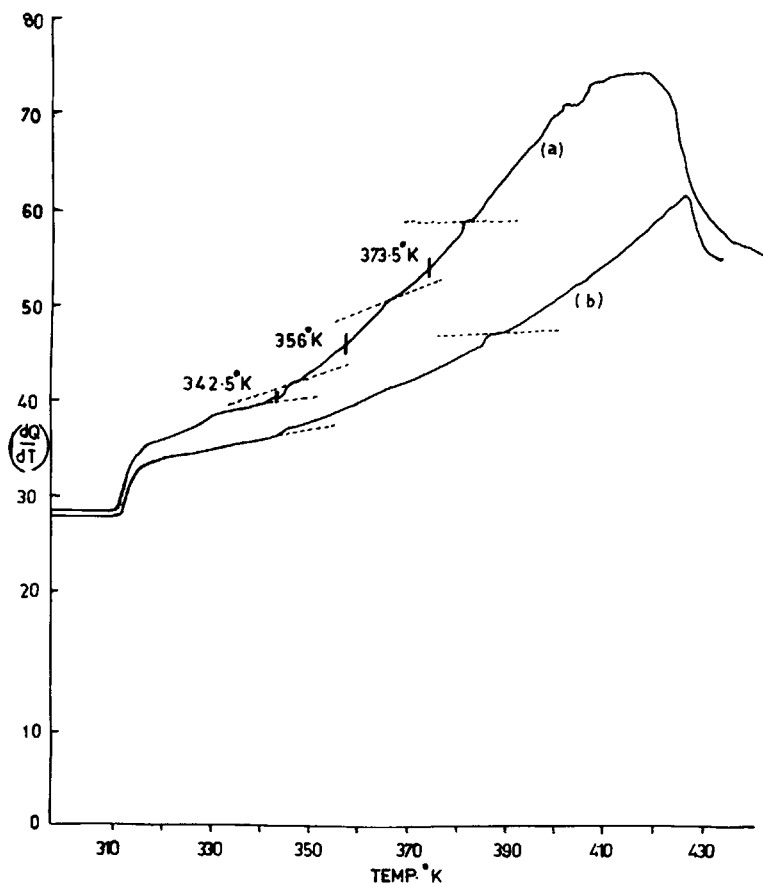


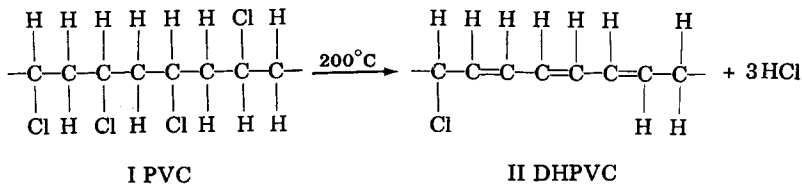
fig. 4 DSC SCANS OF DHPVC-PMMA BLEND
(a) 1st run, (b) 2nd run.

Fig. 4. DSC scans of DHPVC—PMMA blend. (a) First run; (b) second run.

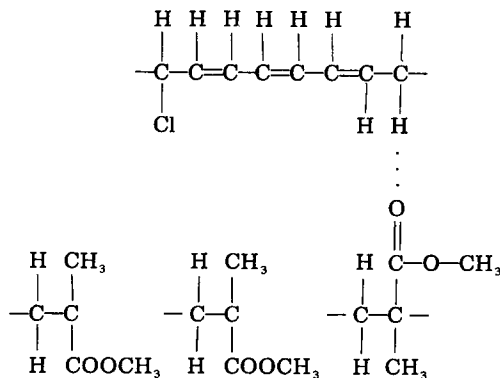
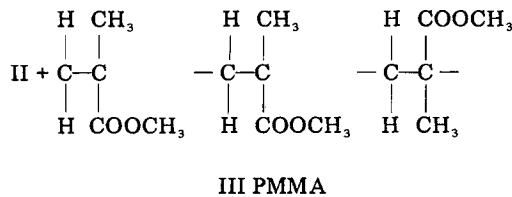
almost unrecognized. It should be stated that the T_g for the blend will recover after a sufficient period of time (5 h). The polymer blend displayed homogeneity with regard to its single glass transition temperature. Results showed that compatibility had occurred between DHPVC and PMMA.

The theoretical background for the compatibility of DHPVC and PMMA was as follows:

The thermal modification in PVC was carried out by thermal degradation, at the temperature of 200°C. The degree of unsaturation was limited by the stabilizers which accept or scavenge hydrogen chloride, preventing further degradation by heat.¹⁵ As per the UV spectral analysis, the extension of conjugated double bond was up to three monomers in a sequence. Assuming that the methylene proton was initially susceptible for dehydrochlorination by free radical mechanism, the following structures I and II were proposed:



The degradation with simultaneous introduction of allylic activation in PVC led to some interactions with neighboring PMMA:



The reactivity of the methylene present in DHPVC towards the neighboring chlorine in the C—Cl bond to form a hydrogen bond was not favorable from the geometrical considerations.¹⁶ The methylene present in the DHPVC was highly active enough to attract a large ester group present in the PMMA to form a hydrogen bond. The structural form of PMMA was “atactic.” It was concluded by NMR spectral data (Fig. 5). The observed responses were tabulated in Table

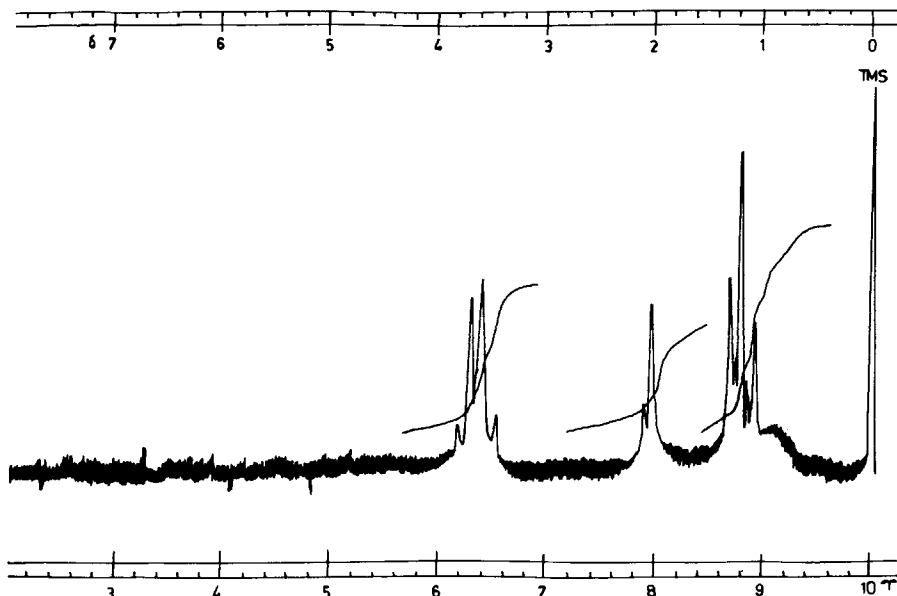


Fig. 5. NMR spectra of PMMA in CCl_4 (25°C , 60 MHz), 500 Hz sweep width.

II. The structural orientation of PMMA (atactic) also favored the formation of hydrogen bonding. In another sense, the random orientation of ester group in PMMA, properly articulated spatially, favored the formation of hydrogen bonding. Several kinds of multiple bond formation like intersequence and in-trasequence could be contemplated, and the details were seen elsewhere.¹⁷

The thermodynamic explanation for the mixing of DHPVC and PMMA was as follows:

According to thermodynamics¹⁸ $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$. The free energy of mixing for the polymer blend was as follows: The molecular weights (\bar{M}_v) of PVC and PMMA were 6.871×10^4 and 6.106×10^5 , respectively. The dispersion of PMMA in PVC at this level was difficult, because ΔS would be negative for mixing of high molecular weight polymers.¹⁹ However, the composition of PVC and PMMA was in the ratio of 74.28:25.72. The change in enthalpy of mixing was considered to be addition of dispersive ($\Delta H_{\text{mix}}^{\text{dis}}$) and specific interaction ($\Delta H_{\text{mix}}^{\text{sp}}$):

$$\Delta H_{\text{mix}} = \Delta H_{\text{mix}}^{\text{dis}} + 11\Delta H_{\text{mix}}^{\text{sp}}$$

where 11 = the number of interactions which were hydrogen-bonding. Since

TABLE II
Observed Responses in NMR Spectra of PMMA

Absorption		Responses	Probable assignment
6.3 τ } 6.42 τ }	—O—CH ₃	strong } strong }	—O—CH ₃ protons; shift due to the influence of adjacent oxygen atoms
8.0 τ	CH ₂	one strong and one weak	Syndiotactic (rrr triad) and atactic (mrr triad)
8.68 τ } 8.82 τ } 8.93 τ }	—CH ₃	appreciable strong appreciable	isotactic heterotactic syndiotactic } atactic

($\Delta H_{\text{mix}}^{\text{sp}}$) was negative for the formation of hydrogen bonding due to interaction, whereas ($\Delta H_{\text{mix}}^{\text{dis}}$) was positive, ΔH_{mix} would be an exothermic constituent of sufficiently low positive value. Therefore, the change in free energy of mixing would be negative. The thermodynamic explanation based on hydrogen bonding also satisfied for the mixing of DHPVC and PMMA.

CONCLUSION

The impact-resistant DHPVC—PMMA foam was synthesized by introducing compatibility during the stage of foaming. The compatibility was confirmed by UV, IR, and DSC techniques. A quantitative study of unsaturation present in DHPVC—revealed 3.0% monomer units with double bond and active methylene group sites. The DSC analysis showed a single T_g of 69.5°C for the polymer blend, DHPVC—PMMA. An explanation was given for mixing on the basis of hydrogen bond formation. The thermodynamic views were also correlated. The versatility of this method lies in the fact that incompatible polymers can also be blended by introducing some structural changes or by creating some active sites. The synergic properties of the two polymers play an important role in some special applications. The foam prepared in this laboratory utilized the rubbery nature of PVC and the brittle nature of PMMA to get the synergic property of impact resistance. The impact resistance is the immense need for any insulating material to withstand the shock and thrust during ascent and descent of the space vehicle, and the same was achieved in the present foam by polymer blending.

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