

Ultrasonic velocity and absorption on methylmetha acrylic resins

C RAKKAPPAN, A SRINIVASA RAO and B KRISHNAN*

Raman School of Physics, Pondicherry University, JIPMER campus, Pondicherry 605 006, India

MS received 26 April 1989; revised 22 July 1989

Abstract. Ultrasonic velocity and absorption were studied in autocure and heatcure resin monomers at different temperatures. Ultrasonic velocity increased in the autocure sample while absorption was reduced. This is attributed to the presence of certain structural factors such as hydrogen bonding.

Keywords. Ultrasonic velocity; absorption; hydrogen bonding.

1. Introduction

Ultrasonic velocity and absorption studies in organic liquids have proved to be useful in understanding their physico-chemical behaviour. In dentistry, synthetic resins are employed for the restoration of missing teeth structures. The synthetic resin most widely used in dentistry is that based on acrylic resin polymethyl methacrylate (PMMA). Ultrasonic studies in PMMA (Asay *et al* 1967, 1969) and its solution (Nomura *et al* 1969; Funfschilling and Lemarchal 1970; Singh 1973) have been reported earlier. But polymethyl methacrylate by itself is not used in dentistry; rather, the liquid monomer is mixed with the polymer to form a plastic dough. There are two types of resin monomers (methylmethacrylate) used in dentistry, viz., heatcuring acrylic resin and chemically-activated acrylic resin or selfcuring or autopolymer resin. Methylmethacrylate is a clear transparent liquid and is an excellent organic solvent. In heatcuring acrylic resin, the monomer is generally pure MMA and in the chemically-activated resin a small amount of tertiary amine is added to the monomer. The addition of these resin monomers to PMMA may alter the elastic properties of PMMA. Hence it is worthwhile to study the elastic properties of these resins separately. Such studies are scanty in literature (Papayoanou and Christopoulos 1973). The present investigations were therefore undertaken to study the ultrasonic velocity and other parameters of these samples.

2. Experimental

Commercial grade (Stellon RR) monomers were used. The ultrasonic velocity and absorption were measured using a pulse echo interferometer (10 MHz, System Dimensions, Bangalore) by the standard procedure (Srinivasan *et al* 1975). Accuracies

* For correspondence

in the measurement of velocity and absorption are 0.01% and 3% respectively. The substance was taken in a specially fabricated cell (Mallikharjuna Rao 1988). Constant temperature was maintained by circulating water from the thermostatically-controlled ($\pm 0.1^\circ\text{C}$) water bath. Absorption is expressed in $\text{Np m}^{-1} \text{s}^2$ and densities at various temperatures were determined using a dilatometer, with an accuracy of 0.005%. The coefficient of volume expansion (v) was calculated from the volumes measured using the same calibrated dilatometer (accuracy 1.5%). Viscosity was estimated using a viscometer (Ostwald) which was kept in a constant temperature water bath (accuracy 0.04%).

3. Physical parameters

The various physical parameters were calculated from the measured values of ultrasonic velocity (C), density (ρ) and the coefficient of volume expansion (v) using the standard formulae.

- (i) Adiabatic compressibility: $\beta_s = 1/C^2 \rho$.
- (ii) Internal pressure: $P_i \gamma = T v / \beta_s$ where γ is the ratio of specific heat capacities.
- (iii) Intermolecular free length: $L_f = K \beta_s^{1/3}$. The values of K for different temperatures were taken from the work of Jacobson (1954).
- (iv) Classical absorption: $(\alpha/f^2)_{\text{class}} = 8\pi^2 \eta_s / 3\rho C^3$.
- (v) Excess absorption: $(\alpha/f^2)_{\text{excess}} = (\alpha/f^2)_{\text{obs}} - (\alpha/f^2)_{\text{class}}$.

4. Results and discussion

The various parameters listed above have been calculated and are presented in tables 1 and 2. The ultrasonic velocity of the autocure resin monomer is higher than that of the heatcure resin monomer at all temperatures. Ultrasonic velocity decreases as temperature is increased in both the resin monomers.

Adiabatic compressibility increases with increase of temperature in the two resin monomers. The autocure resin has less compressibility as compared to the heatcure resin monomer at all temperatures.

Internal pressure $P_i \gamma$ decreases in both cases with increase of temperature and the intermolecular free length L_f increases.

But the observed absorption (α/f^2) is higher in the case of the heatcure resin monomer with no significant difference in classical absorption in the two different types of monomers. Absorption was studied at 303, 313 and 323 K only.

It can be seen from the table 1 that compressibility in the autocure sample at any given temperature is always less than that of the heatcure sample. The fact that L_f decreases indicates that the molecules are very close in the autocure sample. This is also reflected in the internal pressure. As compared to the heatcure sample the autocure sample contains a tertiary amine group which provides additional hydrogen bonding thus not only strengthening the intermolecular forces resulting in a decrease of compressibility but also increasing the velocity in the autocure sample (Anbananthan *et al* 1975; Nambinarayanan and Srinivasa Rao 1979). It is known that internal pressure is increased in a hydrogen bonded system (Velmourougane and Krishnan 1987).

As temperature increases, velocity decreases. This is to be expected as

Table 1. Ultrasonic velocity and related parameters for autocure and heatcure monomers.

| Temperature (K) | 293 | 303 | 313 | 323 |
|--|--------|--------|--------|--------|
| Ultrasonic velocity (ms^{-1}) | | | | |
| Autocure | 1200 | 1182 | 1142 | 1117 |
| Heatcure | 1194 | 1175 | 1132 | 1094 |
| Density (kg m^{-3}) | | | | |
| Autocure | 945.00 | 933.32 | 920.50 | 910.20 |
| Heatcure | 947.50 | 937.05 | 927.88 | 917.63 |
| Adiabatic compressibility ($\beta_s (\times 10^{-10}) \text{N}^{-1} \text{m}^2$) | | | | |
| Autocure | 7.348 | 7.669 | 8.330 | 8.806 |
| Heatcure | 7.403 | 7.730 | 8.410 | 9.105 |
| Internal pressure ($P_{ij} (\times 10^3) \text{atm}$) | | | | |
| Autocure | 5.1234 | 5.0146 | 4.7032 | 4.5404 |
| Heatcure | 4.2356 | 4.1550 | 3.9017 | 3.6779 |
| Intermolecular free length ($L_f (\text{\AA})$) | | | | |
| Autocure | 0.5315 | 0.5326 | 0.5859 | 0.6118 |
| Heatcure | 0.5335 | 0.5548 | 0.5888 | 0.6222 |

Table 2. Ultrasonic absorption and related parameters for autocure and heatcure monomers.

| Temperature (K) | 303 | 313 | 323 |
|---|---------|---------|---------|
| $(\alpha/f^2)_{\text{obs}} (\times 10^{15} \text{Np m}^{-1} \text{s}^2)$ | | | |
| Autocure | 186 | 230 | 387 |
| Heatcure | 224 | 269 | 391 |
| Viscosity (η_s poise) | | | |
| Autocure | 0.05371 | 0.04774 | 0.04065 |
| Heatcure | 0.05490 | 0.04988 | 0.04191 |
| $(\alpha/f^2)_{\text{class}} (\times 10^{15} \text{Np m}^{-1} \text{s}^2)$ | | | |
| Autocure | 9.17 | 9.16 | 8.43 |
| Heatcure | 9.50 | 9.34 | 9.18 |
| $(\alpha/f^2)_{\text{excess}} (\times 10^{15} \text{Np m}^{-1} \text{s}^2)$ | | | |
| Autocure | 176.8 | 220.8 | 378.6 |
| Heatcure | 214.5 | 259.3 | 381.8 |

intermolecular forces are weakened due to thermal agitation. For the same difference of temperature the autocure sample shows a smaller difference in velocity as compared to the heatcure sample. This also indicates that autocure samples are more strongly bonded.

There is no significant difference in classical absorption in both monomers. But the observed absorption is about 20 times the value of the classical absorption in both samples, indicating that the absorption is not due to shear viscosity alone but is mainly dependent on structural aspects. From the structure of the monomer, the hydrogen bond can be identified as a structural factor. The absorption observed at any given temperature is less for the autocure sample than for the heatcure sample. The autocure sample contains dimethyl *p*-toluidine tertiary amine which gives additional hydrogen-bond strength as compared to the heatcure sample. A decrease in absorption due to the addition of triethyl amine to certain liquids have been reported (Prabhakara Rao and Reddy 1977). It is known that in tertiary amine there is rotational isomerism (Blandermer 1973). The observed decrease of absorption in autocure sample may be due to hindered rotational effect (Herzfeld and Litovitz 1959).

Acknowledgments

The authors thank Dr T K Nambinarayanan and Dr K Srinivasa Manja for helpful discussions. Thanks are also due to Dr Senthilkumar, Raja Muthiah Dental College, Annamalai University, for useful suggestions.

References

- Anbananthan D, Krishnan B and Srinivasa Rao A 1975 *Indian J. Chem.* **13** 512
Asay J R, Lamberson D L and Guenther A R 1967 *J. Appl. Polym. Sci.* **11** 1087
Asay J R, Lamberson D L and Guenther A R 1969 *J. Appl. Phys.* **40** 1768
Blandermer M J 1973 *Introduction to chemical ultrasonics* (London: Academic Press)
Funfschilling O and Lemarchal P 1970 *C.R. Acad. Sci.* **C170** 659
Herzfeld F K and Litovitz T A 1959 *Absorption and dispersion of ultrasonic waves* (New York: Academic Press)
Jacobson B 1954 *Nature (London)* **173** 772
Mallikharjuna Rao P 1988 *Ultrasonic studies in binary, ternary systems and liquid crystals*, Ph D thesis, University of Madras, Madras
Nambinarayanan T K and Srinivasa Rao A 1979 *Curr. Sci.* **48** 203
Nomura H, Kato S and Miyahara Y 1969 *Nippon Kagaku Zasshi* **90** 250
Papayoanou A and Christopoulos J A 1973 Research and development technical report ECOM-4142, United States Army Electronics Command, Fort Monmouth, New York
Prabhakara Rao N and Reddy K C 1977 *Pramāṇa - J. Phys.* **8** 245
Singh R P 1973 *Proc. Nucl. Solid State Symp.* **C16** 250
Srinivasan K R, Krishnan S, Srivaraman A, Nagarajan N, Ramakrishnan J and Gopal E S R 1975 *Proc. Symp. Transducer Technology* (Cochin: NPOL) pp. 283-290
Velmourougane S and Krishnan B 1987 *Indian J. Phys.* **B61** 105