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Structure-Properties Correlation in Copolymers of Methyl Methacrylate & Alkyl Methacrylates

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ABSTRACT

The results of a study on the copolymerisation of methyl methacrylate (MMA) with varying mol fractions of octyl methacrylate, decyl methacrylate (DMA), lauryl methacrylate (LMA) and stearyl methacrylate (SMA) by free radical polymerisation using benzoyl peroxide as the initiator are presented. It was anticipated that incorporation of alkyl methacrylate (AMA) having a long alkyl side chain in poly(methyl methacrylate) (PMMA) backbone may lead to an improvement in the toughness of the cast sheets. Such copolymers can be used for low temperature applications in defence.

The glass transition temperature of the polymers determined using differential scanning calorimetry was found to decrease with increase in length of the alkyl side chain and the comonomer content. A significant increase in percentage elongation and decrease in tensile strength, modulus and per cent transmittance was observed on incorporation of AMA in PMMA backbone. In the copolymers of SMA and MMA, significant opacity was observed.

1. INTRODUCTION

Varma and coworkers[1-8] reported copolymerisation and thermal behaviour of methyl methacrylate (MMA) with several vinyl monomers. The effect of alkyl group and structure of the side chain on physico-mechanical properties of cast acrylic sheets was also studied[6].

The present study was aimed at investigating systematically the effect of length of the side chain in alkyl methacrylate (AMA) and copolymer composition on the properties of MMA copolymers. It was anticipated that internal plasticisation due to the presence of long alkyl side chain would lead to an improvement in toughness of the cast sheets without significantly affecting the useful optical and mechanical properties. Such cast sheets may be used for low temperature applications in defence. Several copolymer sheets were therefore prepared by copolymerising 0.05-0.25 mol fractions of octyl methacrylate (OMA), decyl methacrylate (DMA), lauryl methacrylate (LMA) and stearyl methacrylate (SMA) with MMA. The effect of length of the alkyl side chain and comonomer content on percentage

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transmittance, mechanical properties and softening temperature was evaluated.

2 EXPERIMENTAL DETAILS

2.1 Materials

Methyl methacrylate (MMA, Aldrich) was purified by washing with 10 per cent $NaOH$ solution followed by water. MMA was left overnight over anhydrous Na_2SO_4 and distilled under reduced pressure. OMA, DMA, LMA and SMA were synthesised in the laboratory by esterifying methacrylic acid with corresponding alcohol using *p*-toluene sulfonic acid as catalyst. Benzoyl peroxide (BPO) was recrystallised from chloroform solution.

2.2 Preparation of Prepolymer Syrup

To fabricate sheets, a prepolymer syrup was prepared by taking requisite quantities of MMA and comonomers in a round bottom flask fitted with a nitrogen inlet and a reflux condenser. Nitrogen gas was bubbled through the solution and then 1 per cent (w/w) BPO was added. The temperature was then raised to 75 °C. When the extent of conversion was ~ 15 per cent, the flask was removed and the reaction was arrested by quench-cooling the contents of the flask in ice water.

2.3 Preparation of Mold

Two-toughened glass plates (21.5 x 29.0 cm^2) were cleaned thoroughly and sprayed with a silicon release agent. A polyvinyl chloride (PVC) gasket of 2 mm diameter was placed in between the plates which were held together by using steel clamps. One side of the mold was kept open for pouring the prepolymer syrup.

2.4 Fabrication of Sheets

About 100 ml of monomer—polymer syrup—was used for fabricating sheets, because it reduces the amount of heat to be dissipated, reduces the probability of trapped air bubbles, shrinkage and also lowers the initiation temperature. After filling the glass mold with the prepolymer syrup, the opening was closed using a metal plate and clamps. The filled mold was placed in a preheated water bath and the temperature maintained at 75 °C for 4 hr. The assembly was then removed and placed in an air oven at 90 °C for 90 min and then at 120 °C for another 90 min. On the completion of polymerisation, the mold was cooled and solidified acrylic sheets of 18 × 24 × 0.2 cm^3 were taken out by passing a stream of water.

Twenty copolymer sheets were prepared by taking different mol fractions (0.05-0.25) of comonomers (OMA, DMA, LMA and SMA) in the initial feed. All fabricated sheets were free from air bubbles or voids. These sheets have been designated as OMS, DMS, LMS and SMS, respectively. A suffix indicating the mol per cent of comonomers taken in the initial feed has been appended to the generic name. For example, a sheet prepared by using 5 or 25 mol per cent of OMA has been designated as OMS-5 or OMS-25, respectively. The feed composition, sample designation and thickness of the fabricated sheets are given in Table 1. Residual monomer content

Table 1. Characteristics of alkyl methacrylate copolymer sheets fabricated

Sample designation	Mole fraction of MMA in feed	Thickness of the sheet (mm)	Intrinsic viscosity (η) (dl/g)	Density at 28+0.1 °C (g/cm^3)
PMMA	1.0000	1.84	1.90	1.176
OMS-5	0.9510	1.88	2.05	1.164
OMS-10	0.9008	1.88	1.95	1.157
OMS-15	0.8528	1.92	1.65	1.131
OMS-20	0.8016	1.89	2.70	1.111
OMS-25	0.7523	1.88	1.94	1.102
DMS-5	0.9501	1.80	2.65	1.162
DMS-10	0.9012	1.82	2.90	1.157
DMS-15	0.8510	1.84	2.05	1.131
DMS-20	0.8001	1.89	2.45	1.122
DMS-25	0.7540	1.89	2.50	1.101
LMS-5	0.9517	1.79	2.75	1.160
LMS-10	0.9012	1.80	2.20	1.153
LMS-15	0.8513	1.86		1.130
LMS-20	0.8031	1.82	2.95	1.109
LMS-25	0.7514	1.80	-	1.018
SMS-5	0.9540	1.80	3.55	1.158
SMS-10	0.9011	1.85	2.85	1.149
SMS-15	0.8516	1.89	2.00	1.140
SMS-20	0.8023	1.88	2.15	1.128

was determined by extracting a small portion of the sheets with methanol for 36 hr using Soxhlet apparatus. The residual monomer was ~ 1.5 per cent in all the copolymers.

3. CHARACTERISATION & TESTING

The intrinsic viscosity of the polymers was determined at 30 ± 1 °C in chloroform using Ubbelohde suspension level viscometer. The copolymer samples in powder form were used for evaluating T_g using DSC technique. The powdered samples were obtained by dissolving small pieces of sheets in chloroform and precipitating the polymer by dropwise addition of this solution into excess of methanol. A DuPont 1090 thermal analyser having a 910 DSC module was used to evaluate the transition temperatures. A sample size of 5.9 ± 0.9 mg and a heating rate of 10 °C/min were used in each experiment. To keep the thermal history of all the copolymers same, the powdered samples were heated in DSC pan to 120 °C at a heating rate of 10 °C/min and this temperature was maintained for 2 min. The samples were allowed to cool and then DSC traces were recorded in a second heating cycle. To characterise the glass transition region, three characteristic temperatures were noted:

T_{on}	Temperature at which deviation from the base line starts. It was obtained by extrapolating the base line and drawing tangent at the steep portion of the curve,
T_f	Post-transition temperature at which the base line becomes straight. It was obtained by extrapolation, and
T_g	Temperature at the inflection point of the transition.

Dynamic mechanical measurements of the copolymer sheets were carried out using Polymer Laboratories dynamic mechanical thermal analyser model Mk II in the range 50-150 °C. A heating rate of 5 °C/min, frequencies of 1 and 10 Hz and a sample size of 30 × 10 × 2 mm^3 were used for recording moduli (storage and loss modulus) as a function of temperature. The D and S alphatometer which is a miniaturised pyranometer, was used to measure solar transmittance of the sheets. Hitachi-330 UV-visible spectrophotometer was used to measure transmittance of the sheets in the wavelength range 300-800 nm.

3.1 Mechanical Properties

The tensile properties were determined according to ASTM D-638 on an Instron tensile tester model-1121 at ambient conditions. For tensile testing, dumb bell-shaped specimens (length 165 mm, width of narrow section 12.5 mm, thickness ~ 2 mm) were used. The edges of the specimens were polished using a fine sand paper. The conditions used for testing were : Gauge length = 50 mm, full scale load = 500 kg, chart speed = 100 mm and cross head speed = 1 mm/min. A minimum of five samples were tested for each composition.

4. RESULTS & DISCUSSION

All the fabricated sheets were transparent and colourless except SMS-20, which was opaque.

The intrinsic viscosity (η) of the copolymers was in the range 1.65-3.5 dl/g (Table 1). The η values showed no systematic trend with copolymer composition. These values were higher than that of the values obtained for copolymers isolated at low conversion[7] (~ 12 per cent), indicating that the polymers formed were of higher molecular weight. This can be attributed to a reduction in the termination reaction at high conversion (~ 98.5 per cent, due to viscosity effect), thereby leading to high molecular weight copolymers. A gel effect above 15 per cent conversion has been reported in MMA homopolymerisation[9]. The density of the copolymer sheets was determined and the results are summarised in Table 1. Density of the copolymers decreased with increase in mol fraction of the comonomers having long alkyl side.

Table 2. Solar transmittance and turbidity values for copolymer sheets

Sample designation	Solar transmittance	Turbidity (τ)
PMMA	0.91	0.052
OMS-5	0.90	0.056
OMS-10	0.89	0.062
OMS-15	0.88	0.066
OMS-20	0.87	0.073
OMS-25	0.87	0.074
DMS-5	0.88	0.071
DMS-10	0.88	0.070
DMS-15	0.87	0.076
DMS-20	0.86	0.080
DMS-25	0.85	0.086
LMS-5	0.88	0.071
LMS-10	0.87	0.077
LMS-15	0.86	0.081
LMS-20	0.86	0.083
LMS-25	0.84	0.097
SMS-5	0.86	0.081
SMS-10	0.82	0.107
SMS-15	0.70	0.189
SMS-20	0.25	0.737

The solar transmittance and turbidity data are summarised in Table 2. A marginal decrease in solar transmittance was observed on copolymerisation of MMA with OMA, DMA and LMA. On increasing the mol fraction of comonomers, a marginal increase in turbidity of copolymer sheets was seen. However, in the case of MMA-SMA copolymers, a significant decrease in percentage transmittance and increase in turbidity was observed even when low mol fractions of SMA were present in the backbone. A copolymer having 15 mol per cent of SMA had 70 per cent transmittance, which was reduced to 25 per cent when 20 mol per cent of SMA was incorporated in poly(methyl methacrylate) (PMMA) backbone. Decrease in transmittance on the addition of higher mol fractions of SMA could be due to incompatibility of PMMA with poly(stearyl methacrylate), which has a non-polar alkyl side chain.

The percentage transmittance of the copolymer sheets at different wavelengths was also measured

Table 3. Percent light transmittance values for copolymer sheets at different wavelengths

Sample designation	Wavelength (nm)							
	360	400	460	500	560	600	660	700
	80.0	83.0	85.5	86.5	87.0	87.0	87.5	88.0
OMS-5	67.0	77.0	81.5	83.2	84.0	86.0	86.5	87.0
OMS-10	75.0	80.2	84.0	85.2	86.2	87.0	87.5	88.0
OMS-15	72.0	77.5	80.5	82.0	82.2	83.0	84.0	84.0
OMS-20	74.0	80.0	83.5	85.0	86.0	86.5	87.5	87.5
OMS-25	67.5	73.0	76.5	78.0	79.0	79.5	81.0	81.0
DMS-5	71.0	78.5	83.0	84.5	85.5	86.0	87.0	87.0
DMS-10	77.0	82.5	85.0	86.0	87.0	87.0	87.1	88.0
DMS-15	70.0	76.0	80.0	81.5	83.0	83.5	85.0	85.0
DMS-20	71.5	77.5	81.0	82.5	83.5	84.0	85.0	86.0
DMS-25	71.0	76.0	80.0	82.0	83.0	83.2	84.0	85.0
LMS-5	78.2	82.5	84.5	85.0	85.8	86.0	86.0	87.5
LMS-10	79.5	82.5	84.5	85.5	86.2	86.5	87.0	88.0
LMS-15	74.0	79.0	82.5	83.5	84.5	85.0	85.5	86.0
LMS-20	78.0	78.2	83.0	86.0	86.5	86.8	87.0	87.0
LMS-25	78.0	82.0	84.4	85.0	86.0	86.0	86.5	86.5
SMS-5	72.0	78.0	82.0	83.0	84.0	85.0	85.5	86.0
SMS-10	67.5	72.2	77.0	78.0	79.5	80.0	81.0	82.0
SMS-15	39.5	45.2	52.0	55.0	59.5	62.0	65.0	67.0
SMS-20	Opaque							

Table 4. Turbidity values for copolymer sheets at different wavelengths

Sample designation	Wavelength (nm) 400	500	600	700
	0.1012	0.0788	0.0756	0.0694
OMS-5	0.1390	0.0978	0.0802	0.0740
OMS-10	0.1173	0.0861	0.0740	0.0679
OMS-15	0.1327	0.1033	0.0970	0.0908
OMS-20	0.1180	0.0859	0.0767	0.0706
OMS-25	0.1673	0.1329	0.1220	0.1120
DMS-5	0.1344	0.0935	0.0837	0.0773
DMS-10	0.1056	0.0815	0.0766	0.0702
DMS-15	0.1491	0.1111	0.0980	0.0883
DMS-20	0.1348	0.1017	0.0922	0.0798
DMS-25	0.1452	0.1050	0.0973	0.0859
LMS-5	0.1074	0.0907	0.0842	0.0778
LMS-10	0.1068	0.0870	0.0805	0.0710
LMS-15	0.1267	0.0969	0.0859	0.0798
LMS-20	0.1351	0.0828	0.0777	0.0765
LMS-25	0.1372	0.0902	0.0837	0.0805
SMS-5	0.1380	0.0902	0.0902	0.0837
SMS-10	0.1760	0.1206	0.1206	0.1072
SMS-15	0.4201	0.2529	0.2529	0.2118
SMS-20	Opaque	-	-	-

Table 5. Glass transition temperatures for copolymer sheets

Sample designation	T_{on} (°C)	T_g (°C)	T_f (°C)
PMMA		114.8	
OMS-5		97.2 (105)	
OMS-10		83.3 (95.3)	
OMS-15		76.9 (86.5)	
OMS-20		58.1 (77.6)	
OMS-25		56.6 (69.3)	
DMS-5		97.0 (99.7)	
DMS-10		80.0 (85.5)	
DMS-15		71.0 (72.4)	
DMS-20		62.0 (60.0)	
DMS-25		55.0 (48.9)	
LMS-5		90.8 (98.9)	
LMS-10		74.3 (84.4)	
LMS-20		55.9 (57.0)	
LMS-25		52.8 (45.0)	
SMS-5		86.9 (—)	

(Table 3). It was low at lower wavelength (400 nm). The turbidity of the copolymers increased with increase in mol fraction of the comonomer (Table 4). The MMA:SMA copolymer sheets showed higher values of turbidity as compared to other copolymer sheets.

The DSC scans of various copolymers are shown in Fig. 1. A shift in base line was observed in the range 45-120 °C, depending on the length of the alkyl side chain of AMA and the mol fraction of comonomers. The characteristic temperatures defining the glass transition range for all the copolymers are tabulated in Table 5. The T_g of fabricated PMMA sheet was found to be 114.8 °C. Incorporation of even low mol fraction (0.05) of comonomers in PMMA backbone resulted in a significant decrease in T_{on}, T_g and T_f values. The decrease in glass transition temperature on incorporation of AMA in PMMA backbone can be explained on the basis of internal plasticisation effect of the alkyl side chain. In MMA-SMA copolymers having higher mol fraction of SMA

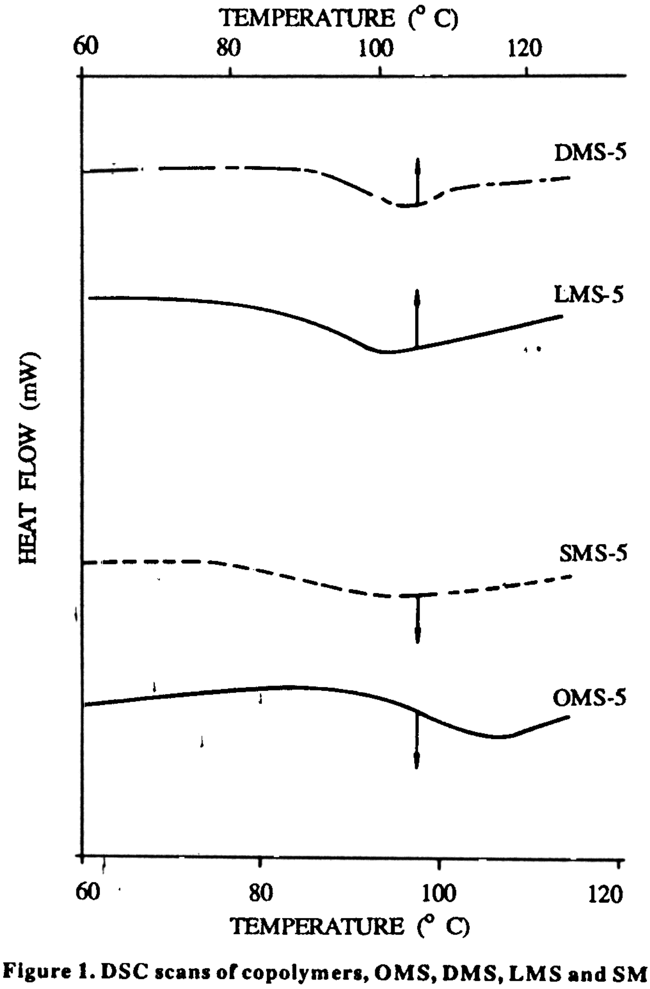

Figure 1. DSC scans of copolymers, OMS, DMS, LMS and SMS

Figures within parentheses represent T_g values calculated using Fox equation in Table 5.

Table 6. Storage modulus and softening temperatures for copolymer sheets

Sample designation	Log E'(Pa) at 0°C		Softening temperature (°C)
	1 Hz	10 Hz	
PMMA	5.5451	5.5694	102.0
OMS-5	5.5347	5.5625	87.0
OMS-10	5.7010	5.7291	66.0
OMS-20	5.2961	5.3543	58.0
OMS-25	5.2694	5.6041	55.4
DMS-5	5.5138	5.5347	78.0
DMS-10	5.5243	5.5555	66.0
DMS-15	5.7568	5.7916	52.0
DMS-20	5.5069	5.5416	50.5
DMS-25	5.5313	5.5763	51.0
LMS-5	5.6527	5.6805	76.0
LMS-10	5.5208	5.5486	68.0
LMS-15	5.4236	5.4652	56.0
LMS-20	5.5624	5.5832	52.0
LMS-25	5.5763	5.6180	48.0
SMS-5	5.5555	5.5833	74.0
SMS-10	5.5486	5.5833	59.6
SMS-15	5.5555	5.5972	49.0
SMS-20	5.2768	5.3324	41.0

(0.10-0.20), the shift in base line was not sharp in DSC scans. Therefore, glass transition temperature could not be determined for these copolymers.

The glass transition temperatures of random copolymers can also be predicted theoretically using the Fox equation:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where

w_1 and w_2 are the fractions of monomer 1 and 2 and T_{g1} and T_{g2} are the glass transition temperatures of homopolymer 1 and 2, respectively. Similar calculation was done in the present work by taking T_g of PMMA as 115 °C and of poly OMA, poly DMA and poly LMA as −20 °C, −60 °C and −65 °C, respectively[10]. The calculated values are given in Table 5.

Figure 2 shows variation in storage modulus (E′) with temperature for OMS-5 copolymer sheet at 1 Hz. Comparison of E′ as a function of copolymer composition showed no definite trend.

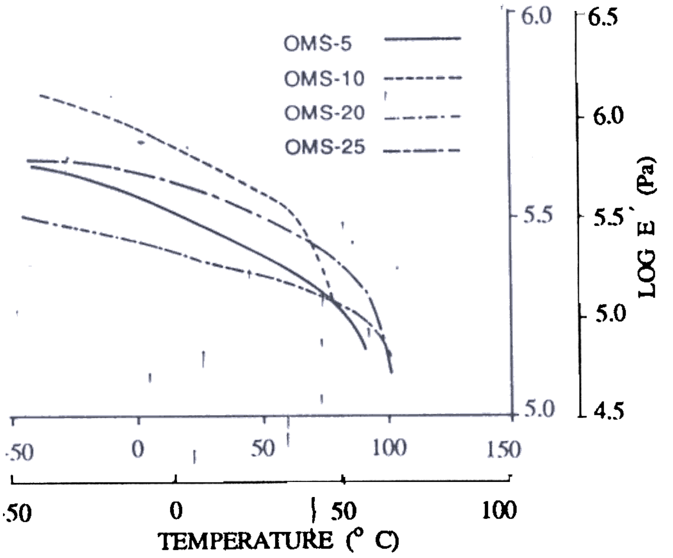

Figure 2. DMTA traces of OMS samples at 1 Hz

The values for storage modulus at 0 °C for different copolymer sheets are given in Table 6. Softening temperature was determined by drawing tangent at the steepest portion of the modulus curve. Softening temperature decreased on incorporation of AMA in the PMMA backbone. It was also observed that increase in comonomer content leads to a decrease in softening temperature of the copolymers. This could be due to decreased intermolecular interactions through incorporation of AMA in PMMA backbone.

The stress-strain curves for SMS copolymers are shown in Fig. 3. From the stress-strain curves, tensile strength at break and at yield, per cent elongation and modulus were calculated and the results are summarised in Table 4. Brittle failure was observed in the case of copolymer samples having 5 mol per cent long chain AMA. Further increase in comonomer content resulted in ductile failure. A significant increase in per cent elongation was observed on adding 15-20 mol per cent long chain of AMA, such as OMA, DMA and LMA. Percentage elongation was much higher in SMS-10, SMS-15 and SMS-20. No significant change in per cent elongation was observed on changing the comonomer from OMA to LMA up to

Table 7. Tensile properties of copolymer sheets

Sample designation	Tensile strength (MPa) at		Strain at break	Modulus	Work of rupture
	Yield	Break	(%)	(MPa)	(MPa)
PMMA	-	61.6	07.6	2100	262
OMS-5	-	56.4	05.6	1670	151
OMS-10	41.0	24.5	12.0	1280	367
OMS-15	32.0	17.0	30.4	780	616
OMS-20	23.0	10.0	33.0	530	439
OMS-25	17.9	8.0	35.0	470	420
DMS-5	-	51.7	06.4	1080	177
DMS-10	43.4	35.0	10.0	1020	446
DMS-15	33.1	15.8	29.7	720	636
DMS-20	26.4	11.2	39.4	690	525
DMS-25	17.2	5.0	54.4	370	327
LMS-5	-	54.4	05.4	1410	111
LMS-10	48.0	44.4	-	1300	460
LMS-15	28.8	16.0	30.0	1000	564
LMS-20	19.2	9.5	63.5	520	446
LMS-25	14.4	6.0	66.6	240	426
SMS-5	-	52.2	04.7	1400	161
SMS-10	34.4	20.0	18.7	1040	428
SMS-15	19.6	10.0	57.9	500	742
SMS-20	12.6	6.2	75.0	290	479

15 mol per cent, whereas a marked increase was observed in LMS-20 as compared to OMS-20. SMS copolymer samples showed higher per cent elongation as compared to other samples. Tensile strength at yield and at break and modulus value decreased with increase in mol per cent of comonomers. Toughness of the copolymer sheets calculated on the basis of area under the stress-strain curve increased with increase in the comonomer content up to 15 mol per cent. These studies thus show that transparent plastics having a strain-to-failure 3-4 times that of PMMA can be prepared by using 10-15 mol per cent of OMA, DMA or LMA as comonomers along with MMA.

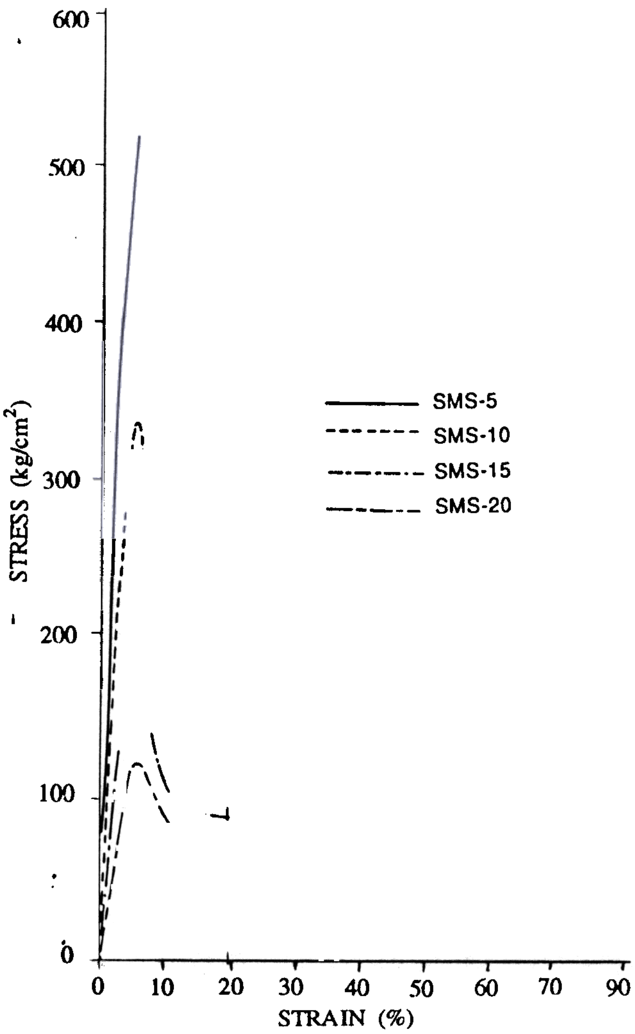

Figure 3. Stress-strain curves of SMS samples

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