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STUDIES ON VISCOELASTIC, THERMAL AND MORPHOLOGICAL PROPERTIES
OF VINYL ESTER – MIXED DILUENTS SYSTEM

Vinyl ester resin networks formed by using mixture of diluents were prepared. Methyl methacrylate (MMA) diluent was mixed in various proportions with vinyl ester resin which was already premixed with styrene diluent (45 wt. %). Weight ratios e.g. 80:20, 70:30 and 60:40 of VE resin: MMA diluents were studied. Viscoelastic properties of the cross-linked resin were studied by dynamic mechanical analyzer in terms of storage modulus and tanδ. Thermal analysis was performed using non-isothermal mode of Differential scanning calorimetry. The samples with mixed diluents, showed higher modulus, and glass transition temperature in comparison to that of the pure vinyl ester-styrene resin cross-linked in presence of styrene only. The difference in thermal stability between vinyl ester-styrene and vinyl ester-MMA-styrene was checked. Vinyl Ester – 20 wt. % MMA-Styrene samples have the best thermal property among all other prepared samples. Multiphase morphology was formed for the thermoset crosslinked with mixed diluents in contrast to that formed with single diluent. With increase in MMA content in the resin dispersed domain size increased.

Keywords: Vinyl ester resin, Dynamic mechanical analysis, TGA, DSC, morphology

1. Introduction

Vinyl ester (VE) resins are extensively used thermosetting resins due to their low cost, outstanding chemical and corrosion resistance, exceptional heat functionality and advantageous mechanical properties over the other thermosets e.g. epoxy and unsaturated polyester resin. Their processability over a broad range of temperature is of critical significance for several end uses, including solvent storage tanks, construction, coating, automobile structural component, swimming pools & marine composites [1]. Vinyl ester resins (VERs) are addition products of epoxide resins and unsaturated carboxylic acids, such as acrylic or methacrylic acids that contain ester groups and carbon-to-carbon double-bond linkages at the end of the polymer chain [2-7]. Curing of Vinyl ester involves free radicle polymerization through the unsaturation on vinyl itself and that of reactive diluents [8].

Several investigators have studied the thermal, viscoelastic and Morphological Properties of VERs, usually with styrene as the reactive diluent. However, the effect of other diluents and their mixtures has not been emphasized much. In the present article the approach is therefore to see the behavior of VER in the presence of mixtures of styrene and methyl methacrylate as the reactive diluents. Concentration of styrene with respect to vinyl ester is kept same throughout but MMA concentration is varied. Characterisation of the cured resin is performed with respect to the MMA wt. %.

2. Experimental procedure

Materials

A commercial available vinyl ester resin (tir@bond 701) was procured from Ruia Chemicals Pvt. Ltd. New Delhi. The physical properties of this resin are given in Table 1.

TABLE 1

Physical Properties of Vinyl Ester Resin
(As Supplied by Manufacturer)

Physical Properties	Vinyl ester resin
Appearance	Pale yellow liquid
Viscosity	400-600 cps @ 25°C
Volatile content	
Acid value	10 ±2 g KOH/gm
Specific gravity	1.06-1.08 @25°C
Gel point	30-35 min @ 82°C

Methyl ethyl ketone peroxide (MEKP), was used as a catalyst and Cobalt naphthenate and N, N^1-Dimethyl aniline (DMA) were used as dual accelerators, respectively. The catalyst & accelerators were procured from Perfect Trading Co., Kolkata, India. Methyl methacrylate monomer (MMA) and sodium hydroxide were procured from Central Drug House, Mumbai, India. Methyl methacrylate monomer was purified by shaking

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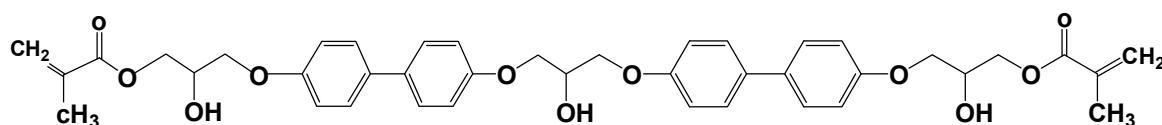
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Fig. 1. Chemical Structure of vinyl Ester Resin

with 2% sodium hydroxide solution in a separating funnel and then washing with water till pH = 7. It was dried over anhydrous calcium chloride, then filtered and stored in refrigerator. Benzoyl peroxide was used as an initiator for acrylate polymerization and was procured from Central Drug House, Mumbai, India. It was used without further purification.

Synthesis of Crosslinkd VERs with mixed diluents

Vinyl ester resin mixed with MEKP, Cobalt naphthenate, and DMA (2 wt. % each) and MMA monomer mixed with 2 wt. % benzoyl peroxide were uniformly mixed in a glass jar. It was left at room temperature till the bubbles disappeared. Casting of the mixture was done into PTFE mould of dimension 215×215×3.3 mm and further kept at room temperature for overnight. Finally curing was done in an air oven at 100°C for half an hour. Test specimens were cut from the samples, wrapped with aluminum foils and kept in desiccators. Pure crosslinked vinyl ester sample was named as VE and VEs mixed diluent of 20, 30 and 40 wt. % PMMA were designated as VEM8, VEM7, and andVEM6 respectively.

The prepared samples were identified using nomenclature as given in Table 2.

TABLE 2

Nomenclature of Prepared Sample

S. No.	Sample composition	Identification
1.	(Vinyl ester resin + styrene) crosslinked	VE
2.	(Vinyl ester resin + styrene + 20% MMA diluent) crosslinked	8VEM
3.	(Vinyl ester resin + styrene + 30% MMA diluent) crosslinked	7VEM
4.	(Vinyl ester resin + styrene + 40% MMA diluent) crosslinked	6VEM

3. Characterization

Physical properties

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the cured vinyl ester resin and Vinyl ester resin with and without mixed diluents in order to find out the exact changes in chemical structure of the resin due to crosslinking reactions. The FTIR analysis was carried out by FTIR prestige-21, Schimadzu Corporation, Japan. The spectra were taken at a resolution of 4 cm^{-1} in ATR mode using KBr pellets and scanning range was 4000 to 400 cm^{-1}.

Density

The density of prepared samples was calculated from below given relationship using the samples weight at air and water medium.

$$Density = \frac{A}{A-B} \times \rho_w^t \qquad (1)$$

where A and B are weights of the sample in air and water, respectively and ρ_w^t is the density of water at the temperature (22°C) during the experiment.

Additionally, the samples densities were calculated using rule of additivity (Eq. 2) to compare between theoretical and experimental values of corresponding.

$$d = d_1 w_1 + d_2 w_2 \qquad (2)$$

Dynamic mechanical analysis

DMA measurements were carried out on a dynamic mechanical analyzer (Q800, TA Instruments). The test specimens of size 35.5×13.5×3.5 mm were tested in a nitrogen atmosphere under a fixed frequency 1.0 Hz (oscillation amplitude 0.03 mm), strain rate of 0.01% and single cantilever mode of sample at a constant heating rate of 5°C/minute from temperature 25-150°C.

Thermal properties

Differential Scanning Calorimeter

Curing behavior of vinyl ester resin with single and mixed diluents was studied by using TA Instruments, USA; model DSC Q$_{10}$ in nitrogen atmosphere (gas flow rate-50 ml/min.) and at constant heating rate 10°C/minute from 0 to 400°C in an aluminum pan crimped with a pinhole. Resin samples were weighed 3-5 mg calibration of the instruments was done with Indium in nitrogen atmosphere using standard procedure.

Thermo-gravimetric Analysis

Thermal stability of the samples was found out by TGA done by DTG-60 (Schimandzu Corporation, Kyoto, Japan), under continuous flow of nitrogen and heating rate of 10°C/min. sample weight was 6-10 mg.

Morphology

Surface morphology of specimens was observed using scanning electron microscope JEOL-JSM 6390 LV, Japan, with the following specifications: accelerating voltage 20 KV; image mode, Secondary electron mode; working distance, 20 mm. The gold coated test samples were mounted to avoid electrical discharging during examination. All samples were scanned into 2000× magnification.

4. Results and discussions

Physical properties

FTIR

The FTIR spectra of VE and VEM samples are shown in Figure 2. The absorption band due to the secondary hydroxyl group are seen at 3420 cm^{-1} and peaks at 1728 and 1170 cm^{-1} are due to carbonyl groups in the methacrylate ester of vinyl ester resins. The absorption peaks at 1650 cm^{-1} and 945 cm^{-1} were due to the stretching and wagging vibrations, respectively, of the C = C in the methacrylate.
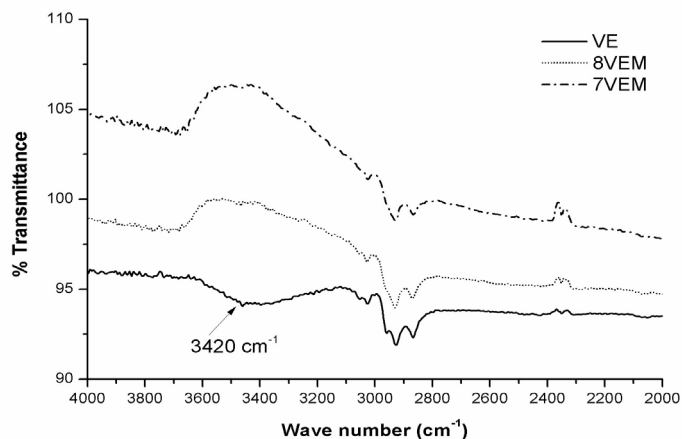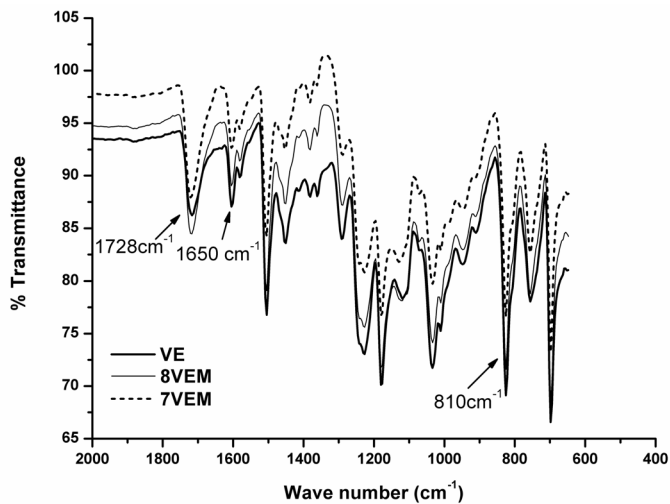

Fig. 2. FTIR spectrum of VE and VEM resins

As crosslinking of VE happens through addition reaction involving C = C bonds progress of the reaction of VE with increasing amount of MMA diluent may be followed by gradual disappearance of the characteristic absorption band due to C = C. With increase in MMA diluent concentration the transmittance peaks corresponding to C = C is decreased which may be attributed to the crosslinking reaction. Also appearance of the peak at 810 cm^{-1} due to methylene (–CH$_2$) of PMMA and vinyl ester [9], is pronounced with increase in MMA content in the sample.

Density

Specific gravity of VE and VEM are shown in Figure 3. The experimentally determined density of the samples follow a reversed trend of variation with increasing concentration of PMMA in comparison to that expected from theoretical calculations. Experimental density of VE is considered as the base for comparison.
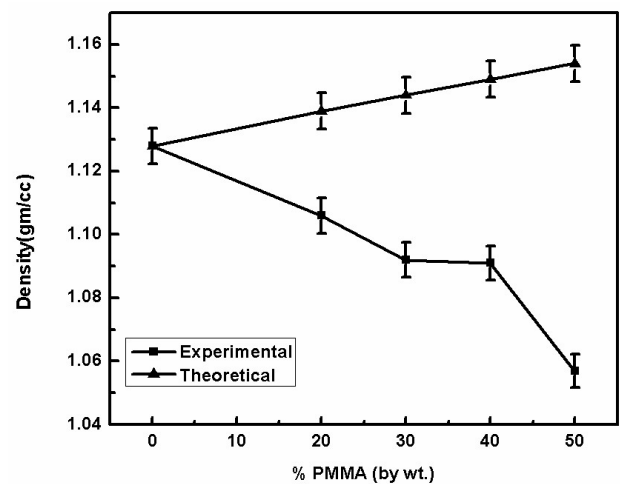

Fig. 3. Variation of density (gm/cc) of VEM resins with the variation of % PMMA content

With increase in the PMMA content density of the VEM samples decreased in practical case. This may be due to the gradual increase in void space in the system upon progressively increased incorporation of two amorphous polymers, PS and PMMA instead of only PS as in VE.

Effect of crosslinking of matrix on viscoelastic properties

It is seen from the Figure 4 that storage modulus of VE is ~12000 MPa at room temperature (30°C) and plateau in the curve between a temperature range of 30-50°C shows elasticity of it. Greater the breadth of the plateau in the low temperature region for a sample, greater is its Hookian elasticity. In the present case VE shows maximum elasticity and 6 VEM shows minimum elasticity. With increase in MMA diluent in the system gradual
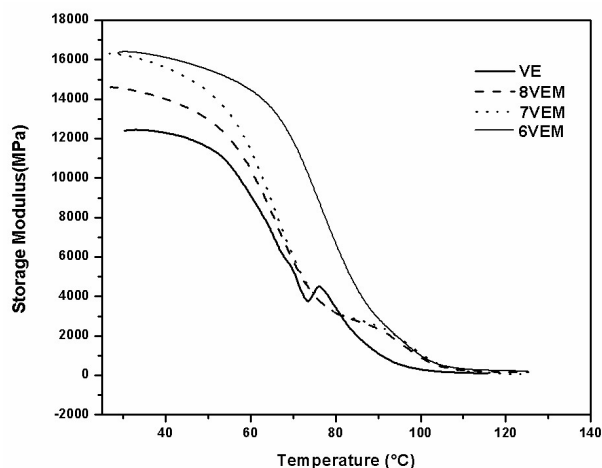
Fig. 4. Variation of Storage modulus (E') of VEMs with temperature

decrease in plateau width is observed in the present case. This may be attributed to the decrease in crosslinking of VE and preferable formation of homopolymer PMMA and copolymers involving MMA, PS and VE. Moreover increased rigid nature of the system, achieved by the formation of rigid, brittle homo and copolymers, may have induced higher storage modulus of VEMs at low temperature range of 30-40°C. Hence instead of toughening of vinyl ester stiffening is found by modification through mixed diluent.
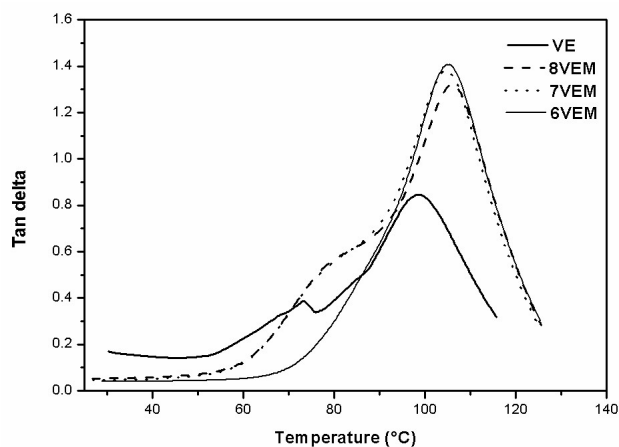

Fig. 5. Variation of tanδ of VEM resins with temperature

In Figure 5 variation of tanδ of VEMs with the variation of MMA content is shown and compared with that of VE with the variation in temperature. With increase in MMA content in the VEMs the tanδ values varied in the order 8VEM < 7VEM < 6VEM. Incorporation of mixed (MMA/styrene) diluent, though has reduced the crosslinking reaction of vinyl ester involving C = C unsaturation-amorphous PS & PMMA (homo and copolymer) the overall disorder in the molecular arrangement is increased due to homo and copolymer formation. Thus the viscous deformation of the VEMs is increased compared to that of elastic deformation and hence higher loss energy for VEMs than that of VE.

Thermal properties

Differential Scanning Calorimetry

DSC thermogram (Fig. 6) of VEMs show glass transition temperature of VE resin at 53°C and that of 8VEM, 7VEM and 6VEM are 54.44, 55.88, and 60.62°C respectively. Higher glass transition temperature of VEMs with respect to that of VE may be attributed to the increased rigidity of the system by the incorporation of in situ formed rigid and brittle polymers, PS and PMMA.
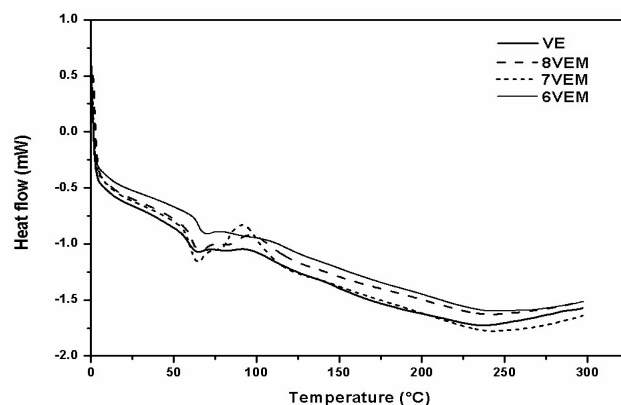

Fig. 6. Overlay of DSC thermogram of (VE/MMA) VEM resins

However, appearance of single glass transition points of all the samples in figure 6 indicates fair miscibility of the component polymers in the VEMs. For such compatible blends, glass transition points (T_g) can be calculated using Fox equation (Hussinaiah et al. 2014) [11], as below:

$$\frac{1}{Tg} = \frac{w_1}{t_{g1}} + \frac{W_2}{t_{g2}} \qquad (3)$$

Where, T_{g1} and T_{g2} represent the glass transition temperature of polymer I and polymer II respectively. Here polymer I is VE and polymer II is VEM. W_1 and W_2 represent their weight fractions in the VEMs. The values are shown in Table 3.

TABLE 3

Glass Transition Temperature of VEMs

Samples	Experimental T_g (K)	T_g from Fox Equation* (K)
VE	326.227	—
8VEM	327.590	335.907
7VEM	329.030	340.960
6VEM	333.770	346.180
PMMA	381.15	—

The values of the glass transition points of the VEMs are expected to be higher with increase in MMA content in them according to Fox equation. The experimental T_g values show the expected trend of variation. However, the transition points obtained by theoretical calculation are higher than the experimental values of corresponding compositions. This may be at-

tributed to the in situ formation of more rigid chains of the homo and copolymers of methacrylate diluent, during crosslinking of vinyl ester, which are accommodated in between the vinyl ester resin chains.

Thermogravimetric Analysis

Table 4 shows data obtained from thermo gravimetric analysis (Fig. 7) of VEM and VE.

TABLE 4

TGA data of VEMs and VE

Sample	T_i (°C)	T_{max} (°C)	T_f (°C)	DTG area (%)	Char yield % 300°C	Char yield % 500°C
VE	319.21	415.58	476.229	96.208	90.90	8.59
8VEM	321.091	415.83	474.878	92.90	93.74	12.25
7VEM	326.148	417.32	479.855	95.77	91.98	8.87
6VEM	317.37	416.085	479.87	90.90	94.52	11.01

T_i = Degradation initiation temperature, T_{max} = Temperature at which maximum degradation occurred, T_f = degradation finish temperature, DTG area means the area under the DTG curve

The thermo-gravimetric (TG) analysis of VE and VEM samples show that the decomposition occurs in two processing steps. First step of degradation (@ around 150°C) may be due to the loss of moisture and residual diluents present [11] and it is seen to remain same (~1-3%) for all the samples. The second step may be attributed to thermal breakage of polymer chains and is seen to vary with the composition variation. With increase in MMA content in VEMs the degradation onset temperature (T_i) is shifted to lower range may be due to formation less crosslinks (dilution effect).

It is exhibited that the initial decomposition temperature (T_i) of VE is marginally lower than that of VEMs. Variation in peak (T_{max}) and final temperature (T_f) of decomposition of these samples was not observed. The area under the DTG curve, which is proportional to total change in weight, was lowest for 8VEM, indicating that the sample was most stable. The char yield at 500°C and at 300°C was highest for the resin 8VEM due to its thermal stability.

Morphology

From the SEM micrographs (Fig. 8) it can be seen that VE shows binary phase morphology where the dispersed phase is very small size and mostly spherical in shape. In 8VEM the morphology of the dispersed phase is somewhat elongated, irregular but distinct boundary between the phases is not observed.
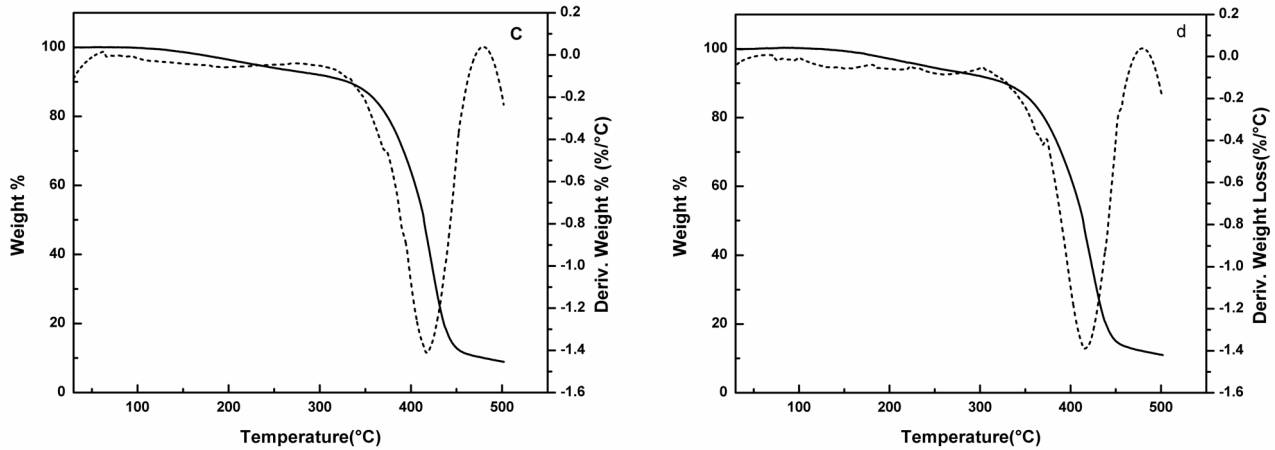

Fig. 7. TGA and derivative thermograms (DTG) of (a) VE (b) 8VEM (c) 7VEM and (d) 6VEM
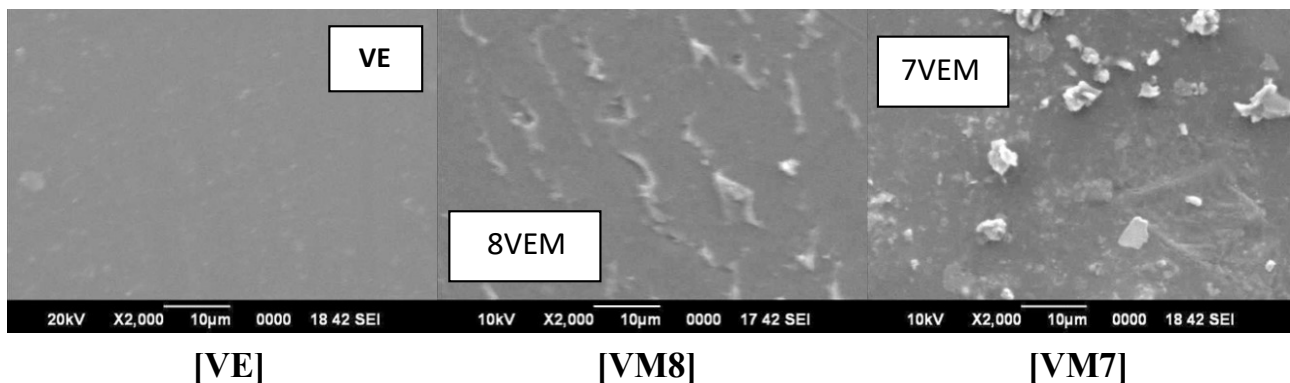

[VE] [VM8] [VM7]

Fig. 8. Scanning Electron Micrographs of VE and VEMs

In 7VEM the morphology is again changed. It is evidenced here that the dispersed phase has irregular shape and distinct phase boundary of the components suggests immiscibility of them.

5. Conclusion

From the thermo-mechanical results, it was found that VE has moderately high elasticity and storage modulus of ~12000 MPa at room temperature (30°C).With increase in MMA content in the VEM the tanδ values varied in the order VE < VM8 < VM7 < VM6. Degree of crosslinking of VE was perhaps reduced as the loss energy was high and elastic behavior of VEM is clear from the reduced breadth of the plateau in Storage modulus vs. temperature curve. DSC results showed that with the increase in MMA content glass transition point of VEMs increased gradually and always a single T_g was exhibited. From TGA results showed that thermal stability of VEMs was neither improved nor deteriorated with respect to that of VE but remained almost same. SEM micrographs exhibited single phase for VE but dual phase for VEMs and with increase in MMA as secondary diluent bigger and irregular domains of dispersed phase observed. Interphase is visible which is showing partial mixing of the components due to which single T_g in DSC was evidenced.

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