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Morphology, mechanical and thermal behavior of acrylate rubber/fluorocarbon elastomer/polyacrylate blends

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Novel thermoplastic elastomers derived from binary and ternary blends of polyfunctional acrylates, acrylic rubber (ACM) and fluorocarbon rubber (FKM) were analyzed by using Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA) and mechanical tests. TEM revealed the presence of a single-phase structure for both acrylate rubber/fluorocarbon elastomer (ACM/FKM) and ACM/polyacrylate binary blends. Increase of FKM concentration in the ACM/FKM/polyacrylate ternary blend resulted in phase separation of FKM from the ternary blend. The FKM formed a dispersed phase with polynodal particle distribution and irregular shape ranging from ellipsoidal to highly elongated form with inclusion of ACM. The FKM/polyacrylate binary blend showed complete phase separation. Ageing of the blend increased the domain size of the dispersed phase. Differential scanning calorimetric (DSC) and DMTA studies showed no major changes in the T_gs of individual polymers in the blend, although the peak tan δ values were affected on changing the composition of the blends. Vulcanization of the thermoplastic elastomer (TPE) changed the phase morphology with increase in particle size. There is a distinct difference in morphology of statically and dynamically vulcanized blends.

1. Introduction

The use of fluorocarbon elastomers (FKM) for industrial application in the form of seals, gaskets, molded goods, hose lining, etc. has grown steadily and gained wide acceptance due to their chemical inertness, heat resistance and stability, and fuel and oil resistance [1]. However due to their high price, proprietary formulation, specific cure systems and difficulty in processing, the fluorocarbon elastomers are limited to high-end applications. Blending of other specialty polymers, which match the properties of FKM, will reduce the cost and improve some of its mechanical properties. Acrylate rubber (ACM) is a suitable candidate to make a blend with fluororubber. It is even better to derive a thermoplastic elastomer from mixing these rubbers with a plastic compatible with either of the rubbers to enhance the processability. Miscibility or compatibility is an important criterion for obtaining a synergistic effect from the blend with appropriate composition [2, 3]. The microstructure or morphology of blends also determines the final properties of such blends. The morphology is determined by many variables such as materials and process parameters. The rheological behavior of multiphase systems is intimately related to their morphology [4, 5], as these components undergo various stages of deformation [6].

The miscibility of polymer blends has been reviewed in many literatures [7–10] and the effect of morphology on physical properties has also been studied extensively by many workers [11–16]. It was found in our earlier work [17] that acrylate rubber (ACM) containing epoxy cure site monomer is miscible with FKM in all blend ratios leading to a synergistic effect in mechanical properties of the gum and filled blends [18].

Blending plastic with rubber or vice-versa is an important technique for obtaining useful products with desirable properties. A high proportion of rubber in a plastic–rubber blend can generate a thermoplastic elastomer, while a low rubber content in the same blend is utilized for improving the impact resistance of plastics. The development of TPE has been reviewed in many literatures. The reactive processing of hydrogenated

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nitrile rubber (HNBR) with Nylon, *in-situ* compatibilisation of low density polyethylene (LDPE) and natural rubber etc. have been reported from this laboratory [19, 20]. Jha and Bhowmick have reported reactive blending of acrylate rubber and Nylon, which shows a synergistic effect on mechanical properties [21]. Inoue *et al.* have discussed morphology of several polymer blends using light scattering and microscopy techniques [22–24].

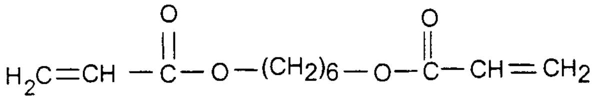
In our earlier work, we reported the mechanical and dynamic mechanical thermal properties of the novel blends of acrylate plastics-ACM/FKM rubber [25]. However, nothing is known about the microstructure of the blends.

The objective of the present work is to prepare thermoplastic elastomer from ACM/FKM/polyacrylate plastic blends having variations in compositions and the nature of the acrylates. These blends have been characterized by Transmission Electron Microscopy (TEM), Differential Thermal Analysis (DSC), Dynamic Mechanical Thermal Analysis (DMTA) and mechanical tests.

2. Experimental

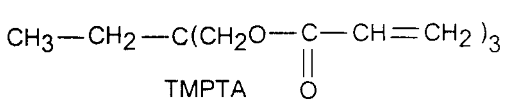
2.1. Materials

Acrylate rubber (ACM), NIPOL AR 51 (density—1100 kg m^{-3} at 25°C, Mooney viscosity ML (1 + 4) at 100°C—55) was obtained from Nippon Zeon Co. Ltd., Tokyo, Japan. Fluorocarbon rubber (FKM), VITON B 50 (density 1850 kg m^{-3}, 68% F, 1.4% H) was supplied by Dupont Dow Elastomers, USA. The acrylate monomers—(i) Hexanediol diacrylate (HDDA, density 1050 kg m^{-3}), (ii) Trimethylolpropane triacrylate (TMPTA, density 1110 kg m^{-3}) and (iii) Dipentaerythritol hexacrylate (DPHA, density 1110 kg m^{-3}) were procured from UCB Chemicals, Belgium. Hexamethylene diaminecarbamate (DIAK #1) was supplied by E. I. Dupont de Nemours & Co., USA. Other chemicals not mentioned above were procured from indigenous sources and were used as such. The molecular structure of the multifunctional acrylates is given below.



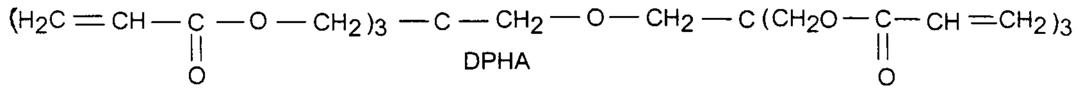
$$H_2C{=}CH-\overset{\overset{O}{\|}}{C}-O-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-CH{=}CH_2$$

HDDA



$$CH_3-CH_2-C(CH_2O-\underset{\underset{O}{\|}}{C}-CH{=}CH_2)_3$$

TMPTA



$$(H_2C{=}CH-\underset{\underset{O}{\|}}{C}-O-CH_2)_3-C-CH_2-O-CH_2-C(CH_2O-\underset{\underset{O}{\|}}{C}-CH{=}CH_2)_3$$

DPHA

2.2. Preparation of the samples

ACM was mixed with FKM in the following blend ratios: 100/0, 70/30, 50/50, 30/70 and 0/100 (w/w) in a Brabender Plasticorder, PLE 330 at 100°C for 5 minutes at a rotor speed of 60 r.p.m. The liquid multifunctional acrylate monomer at an appropriate level was then added slowly in the mixer at the same temperature until the mass became homogeneous (in about 3 minutes). Unless otherwise mentioned, benzoyl peroxide, an initiator for polymerization of acrylates was added, at a level of 0.1% and the mixing was continued for 5 minutes. The torque and temperature were noted for every minute of mixing. It was observed that at 100°C for 5 min in the mixer the acrylate monomers did not polymerise. Hence, a few mixes were prepared at 150°C under identical conditions to compare samples that were polymerised *in-situ* with those of that were polymerised at a latter stage. In order to study the effect of dynamic vulcanisation, the curatives (DIAK #1) were chosen and added along with the acid acceptors ($Ca(OH)_2$ and MgO) and then mixed at 100°C as well as at 150°C. After mixing, the mass was sheeted out at 30°C using a laboratory two roll mill (6″ × 13″ Schwabenthan, Berlin). The samples were then molded in between aluminium sheets in a two plate Hydraulic press (Moore press, UK) provided with cooling circuit at 170°C for 10 minutes at a pressure of 5 MPa. After each molding, the samples were cooled in the press itself to 50°C. The test specimens were cut from the molded slabs of approximately 1.8-mm thickness using ASTM standard cutting dies.

2.3. Measurements

2.3.1. Transmission electron microscopy (TEM)

The morphological studies were performed using transmission electron microscope (HITACHI -HT300) operating at 100 kV. The specimen used for TEM was stained with OsO_4 and a few samples were also stained with RuO_4 for better contrast. The strained samples were cryo-microtomed at −45°C.

2.3.2. Dynamic mechanical thermal analysis

Dynamic mechanical thermal properties of the samples (43.5 × 12.5 × 1 mm) were evaluated on DMTA, RHEOMETRIC SCIENTIFIC MK-II Model under bending dual cantilever mode. The experiments were carried out at a frequency of 1 Hz. The measurements were taken from −50°C to 150°C at a heating rate of 2°C per minute and a double strain amplitude of 64 μm peak to peak displacement. The storage modulus (E') and the loss tangent (tan δ) were measured for all the samples under identical conditions. The data were analysed by using COMPAQ computer and DMTA MK II Software (version 1.2).

2.3.3. Mechanical tests

Tensile specimens were punched out from the molded sheet using ASTM Die-C. The mechanical tests were carried out as per ASTM D412-99 method in a Universal Testing Machine (UTM-ZWICK-1445) at a crosshead speed of 500 mm/min at 25°C. The average value of three tests for each sample is reported here.

2.3.4. Thermal analysis

Thermal analysis was performed on the individual rubbers and the blends using a DUPONT DSC instrument (model No. 2000) attached with automatic programmer. The machine was calibrated with a semiconductor grade indium sample. Approximately 8 mg of the sample was kept inside the sealed aluminium cap. The measurements were carried out in the temperature range from -100 to 100°C at a heating rate of 10°C/min in a nitrogen atmosphere.

3. Results and discussion

3.1. Variation of blend ratio

The compositions of the binary and ternary blends of ACM/polyacrylate, FKM/polyacrylate and ACM/FKM/polyacrylate are shown in Table I. Fig. 1a shows the TEM micrograph of ACM/FKM blend indicating clearly the presence of a single phase and blend miscibility. The binary blend of ACM/p-TMPTA (AT30) does not show any phase separation as shown in the TEM photomicrograph even at a very high magnification (Fig. 1b), representing homogeneous structure. Both acrylate and ACM have similar chemical identity, including the presence of pendant ester group. Due to this, these polymers are compatible with each other. The molded sample prepared from this blend is clear and transparent due to similar refractive indices indicating presence of a single-phase structure.

The morphology of the ternary blend derived from ACM/FKM/p-TMPTA with varying compositions of ACM and FKM at a constant level of p-TMPTA is shown in Fig. 2. The blend containing 70/30 ACM/FKM and poly TMPTA shows phase separation. The dark phase here is the FKM component, which forms a dispersed phase with elongated ellipsoidal particles (Fig. 2a). On the other hand, ACM combines with acrylate to form the continuous phase (bright portion). The average dimensions of the major and minor axis is 0.5–4 μm and 0.2–0.7 μm respectively. The sizes of the dispersed phase show polynodal distribution with varying particle dimension. It is also observed at higher magnification (not shown here) that there is no sharp boundary between the dispersed phase and the matrix. In fact some of the ACM or polyacrylate are also included in the form of islands in the dispersed phase. This may be due to the miscibility of ACM/FKM blend.

Upon increasing the amount of FKM in the ternary blend of ACM/FKM/poly TMPTA to the level of 50/50/30(w/w), the population of dispersed particle per unit area is increased with the retention of phase separated morphology (Fig. 2b). This blend also shows polynodal size distribution. The smaller particles are almost spherical in nature and the bigger particles are presumably formed by the agglomeration of smaller ones during molding leading to irregular shape like elongated spheroids. The inclusion of ACM in FKM domains in this blend is also apparent. The average dimensions of the spherical particles is 0.3–0.6 μm. The morphology is however very stable. Only on ageing at 150°C for 72 h in an air oven, bigger particles through agglomeration of the smaller ones are developed (Fig. 2c).

It is interesting to note that when the FKM concentration is further increased in the ternary blend (30/70/30 blend), more and more dispersed particles combine together and form macrophase leading to the level of co-continuous phase formation (Fig. 2d). If we consider the existence of dispersion of FKM at this blend ratio, the mean size is increased. The spherical or ellipsoidal shape of particles is almost converted into multishaped particles. The polyacrylate still constitutes the matrix and the ACM rubber is now distributed in both the phases. The gradual brightening of the FKM phase in OsO_4 stained samples may be due to coating of ACM on to the FKM phase.

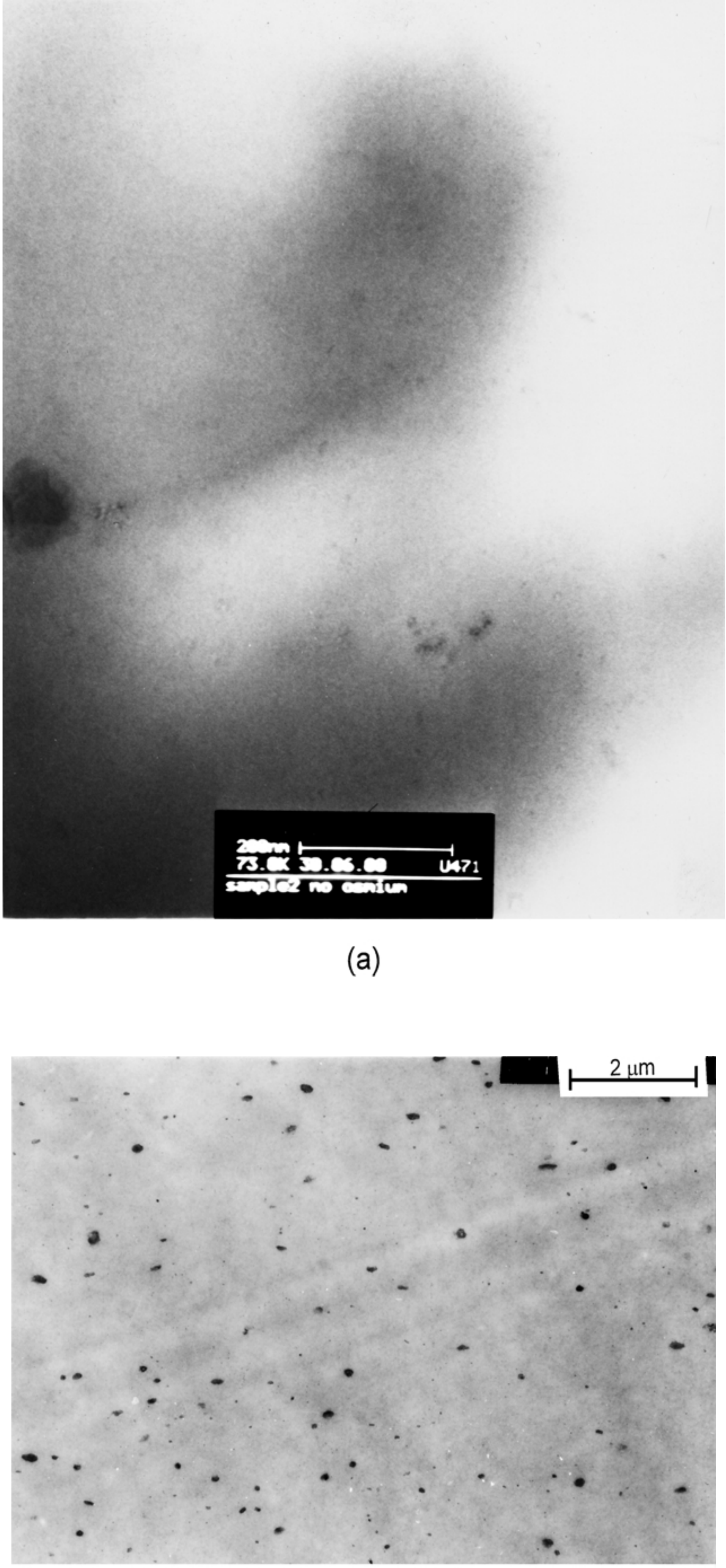
Fig. 2e shows a TEM photomicrograph of FKM/poly TMPTA (FT30) blend. The dark portion represents the FKM phase and the bright portion is again the acrylate phase. As the concentration of the rubber is higher than that of the plastic, the blend behaves like a filled raw rubber. This blend does not show any structured

TABLE I Compositions of thermoplastic elastomers derived from ACM, FKM and acrylates

Sample	AT30	AFT (70/30/30)	AFT30	AFT (30/70/30)		AFH30	AFD30	AFT30 St[a]	AFT30 Dy[b]
ACM	100	70	50	30	FT30	50	50	50	50
FKM	–	30	50	70	100	50	50	50	50
HDDA	–	–	–	–	–	30	–	–	–
TMPTA	30	30	30	30	30	–	–	30	30
DPHA	–	–	–	–	–	–	30	–	–
DIAK #1	–	–	–	–	–	–	–	1.5	1.5
$Ca(OH)_2$	–	–	–	–	–	–	–	3.0	3.0
MgO	–	–	–	–	–	–	–	1.5	1.5

[a] Press cured blend.

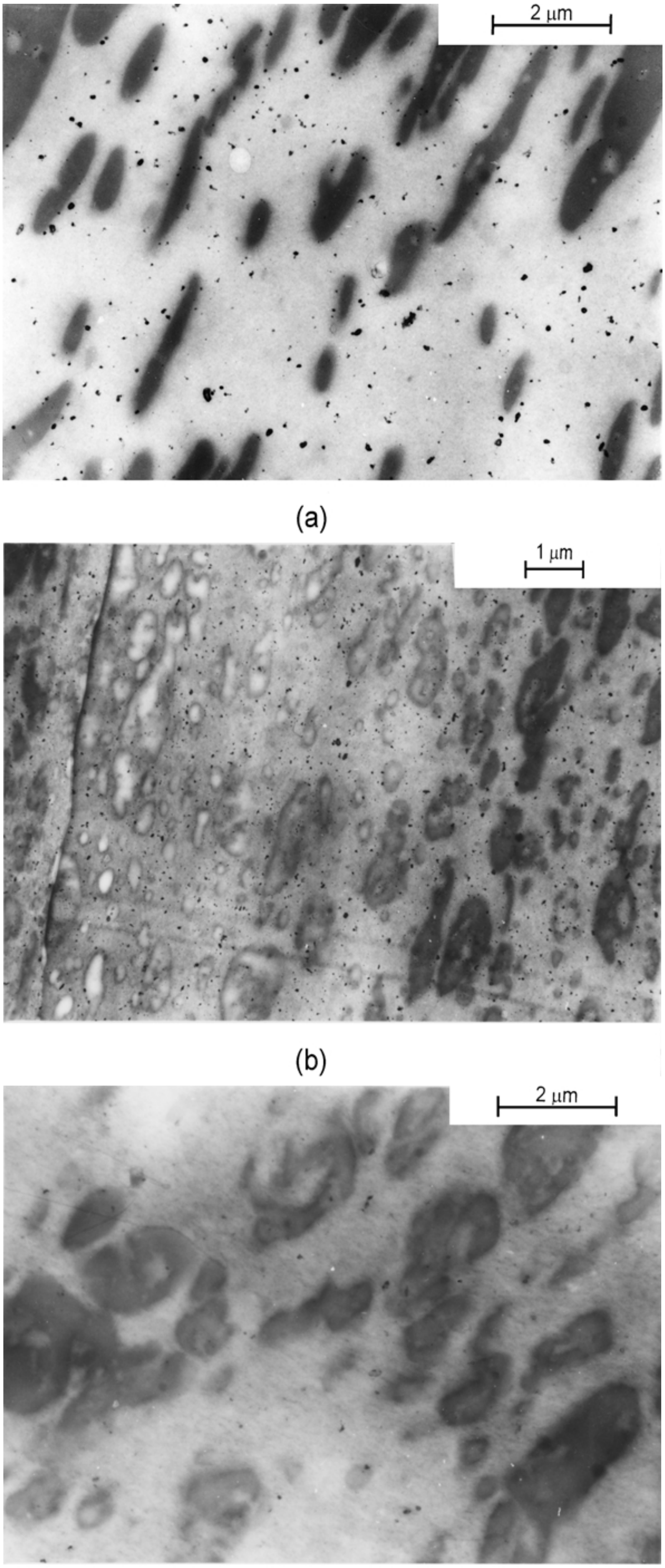
[b] Dynamically vulcanised blend.



(a)

(b)

Figure 1 Transmission electron microphotograph of (a) 50/50 (w/w) ACM/FKM blend and (b) 100/30 (w/w) ACM/p-TMPTA blend.



(c)

Figure 2 Transmission electron microphotograph of (a) 70/30/30 (w/w) ACM/FKM/p-TMPTA blend; (b) 50/50/30 (w/w) ACM/FKM/pTMPTA blend; (c) 50/50/30 (w/w) ACM/FKM/pTMPTA blend after air oven aging; (d) 30/70/30 (w/w) ACM/FKM/pTMPTA blend; and (e) 100/30 (w/w) FKM/pTMPTA blend (*Continued.*)

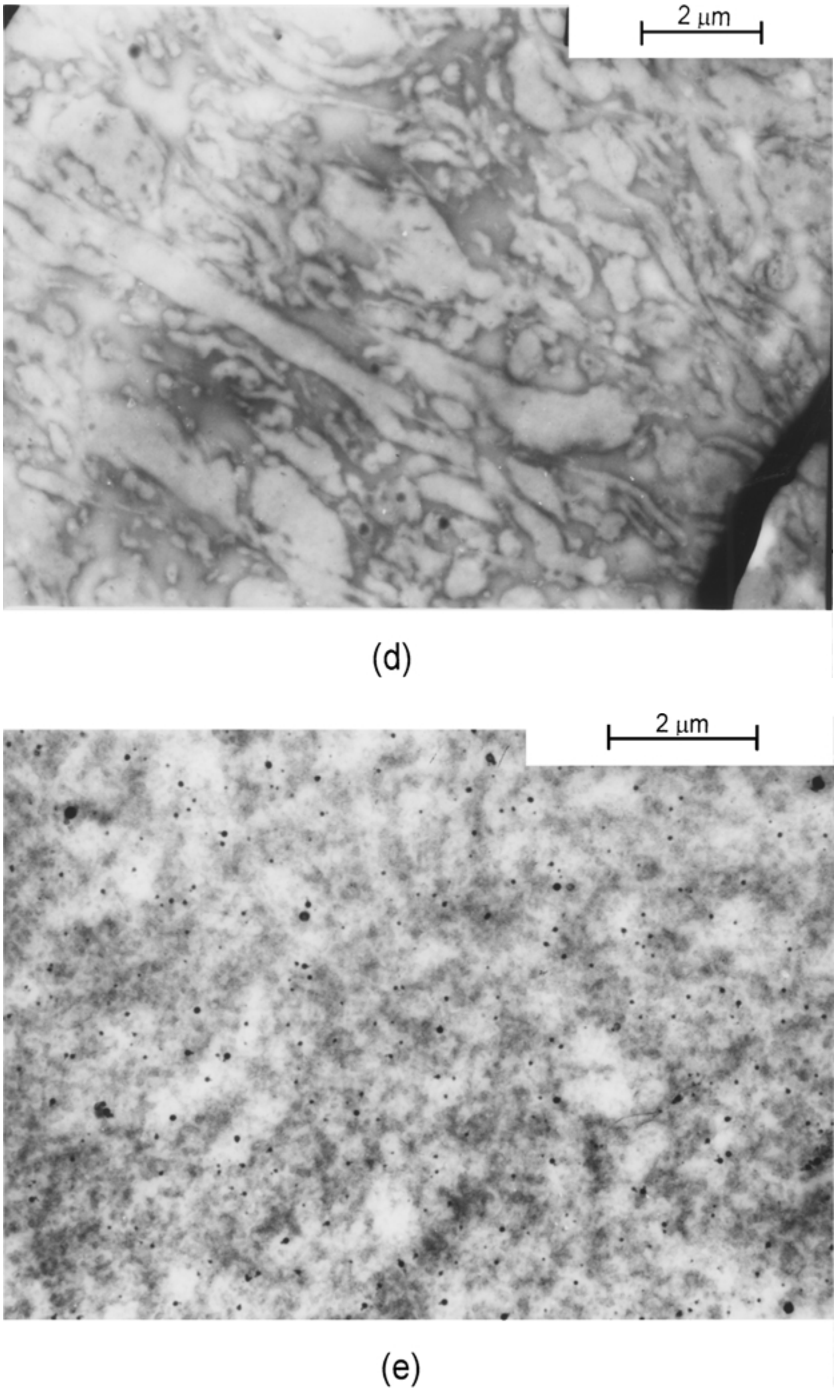


Figure 2 (*Continued.*)

particles of dispersed phase. In order to understand the microstructure through physical measurements, DSC and DMTA experiments have been performed, which are reported in a later section.

The mechanical properties of both binary and ternary blend with varying composition of ACM and FKM are shown in Table II. A correlation between mechanical properties and the phase morphology is attempted here, although such a correlation is a function of many other attributes of the system. The AT30 blend shows tensile strength of 8.5 MPa and the elongation at break of 450%. This may be attributed to the single-phase morphology. The addition of FKM to ACM/p-TMPTA reduces both tensile strength and elongation at break considerably for the 70/30/30 blend. However, further addition of FKM leads to inclusion of ACM in the FKM and less elongated domains leading to increase in modulus and strength.

The 30/70/30 ternary blend shows reduction in tensile properties due to increase in FKM particle dimension which act as a stress raiser leading to poor strength properties. The FT30 shows lowest tensile properties as expected from the above arguments. The gum strength of FKM is 0.4 MPa which is improved to the value of only 3.4 MPa upon the addition of p-TMPTA to FKM. This is mainly attributed to the presence of the continuous polyacrylate phase.

TABLE II Mechanical properties of thermoplastic elastomers

Physical properties	AT30	AFT (70/30/30)	AFT30	AFT (30/70/30)	FT30	AFH30	AFD30	AFT30 St	AFT30 Dy
100% modulus (MPa)	4.3	6.2	7.8	–	3.6	4.7		2.3	7.9
Tensile strength (MPa)	8.5	7.1	9.2	7.3	3.7	6.5	12.8	3.1	8.6
Elongation at break (%)	450	139	138	86	111	270	52	214	118

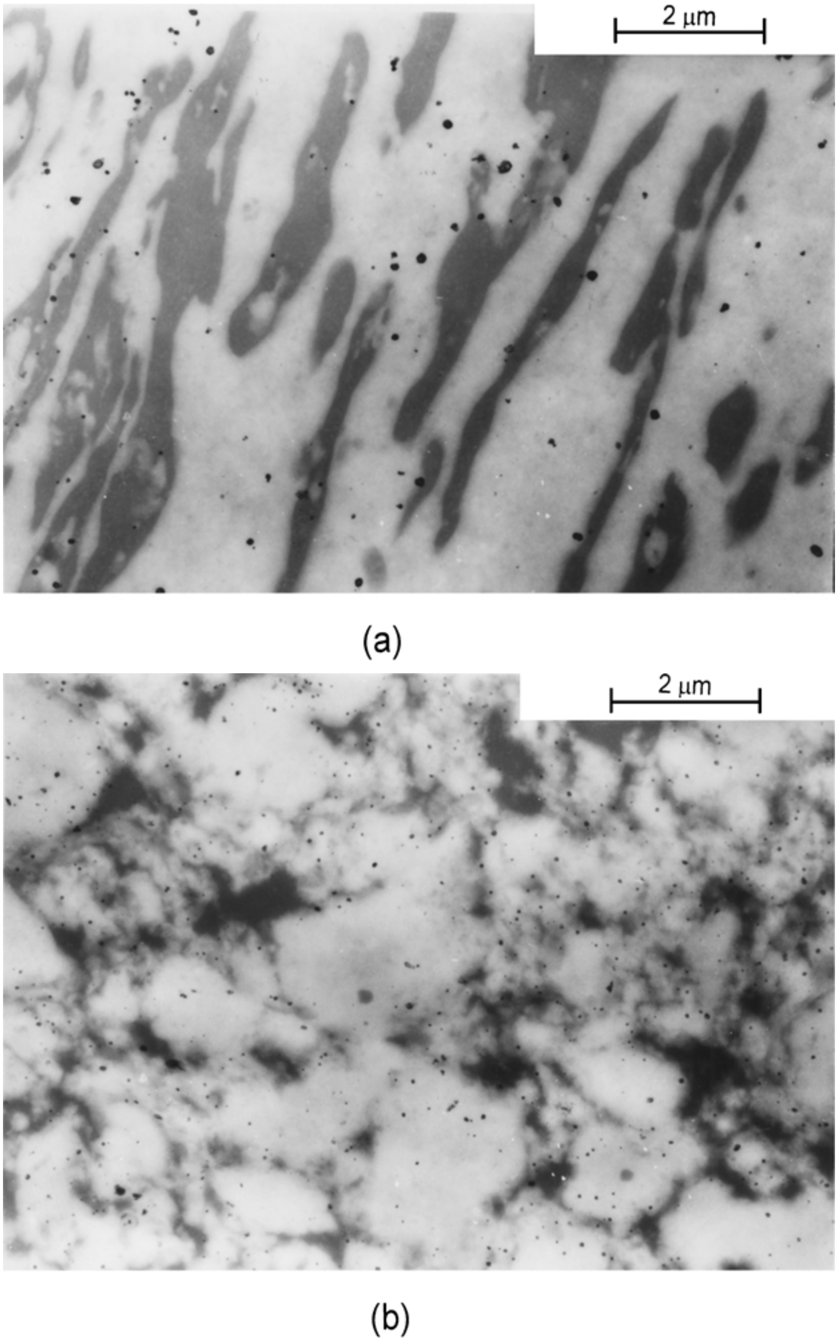


Figure 3 Transmission electron microphotograph of (a) 50/50/30 (w/w) ACM/FKM/pHDDA blend and (b) 50/50/30 (w/w) ACM/FKM/pDPHA blend.

3.2. Variation of nature of acrylate

Acrylates of different multi-functionality, i.e. di-, tri- and hexa-acrylates at the level of 30 phr were evaluated for their influence in phase morphology. The TEM photomicrographs of such blends are represented in Figs 3a, 2b and 3b respectively. Multifunctional acrylates form separate phases. The microstructure of p-HDDA containing blend, AFH30, (Fig. 3a) shows similar phase morphology compared to p-TMPTA containing blend at lower FKM loading. However, there is a difference of particle size and shape of these two blends. AFH30 show highly elongated particles of FKM without definite shape and has high mean diameter. This may be due to easy flow of unvulcanized FKM rubber in p-HDDA/ACM matrix of lower viscosity compared to p-TMPTA (having higher viscosity due to its tri functionality for polymerisation) at the molding condition. This blend also shows the formation of ACM/polyacrylate islands in the FKM domain.

On the contrary, the corresponding TEM picture of p-DPHA (hexa functional acrylate) containing blend shows complete phase separation between FKM (dark region) and acrylate. The magnitude of particle size is so high (in micrometer level) that it leads to poor stress transfer under applied load condition. The absence of elongated dispersed particle in this blend (as seen in the case of the p-HDDA containing blend) may be due to the inability of FKM rubber to undergo deformation in a highly viscous hexa-acrylate matrix during molding. In addition DPHA undergoes crosslinking and cyclization along with polymerisation in the presence of ACM/FKM blend leading to higher matrix viscosity compared to either di- or tri- acrylates.

It is inferred from this study that the change in the multi-functionality affects the microstructure development during molding which gives rise to variation in the mechanical properties. It is a well-known that the strength of a blend is correlated with the nature and size of the domain in a multiphase polymer blend. As the dimension of dispersed phase is increased, the tensile property will go down. This fact is reflected in the study of variation of nature of acrylates (Table II). The moderate tensile strength and higher elongation of AFH30 confirms the prediction of phase morphology having elongated particles, which take care of higher elongation. It is cautioned here however, that

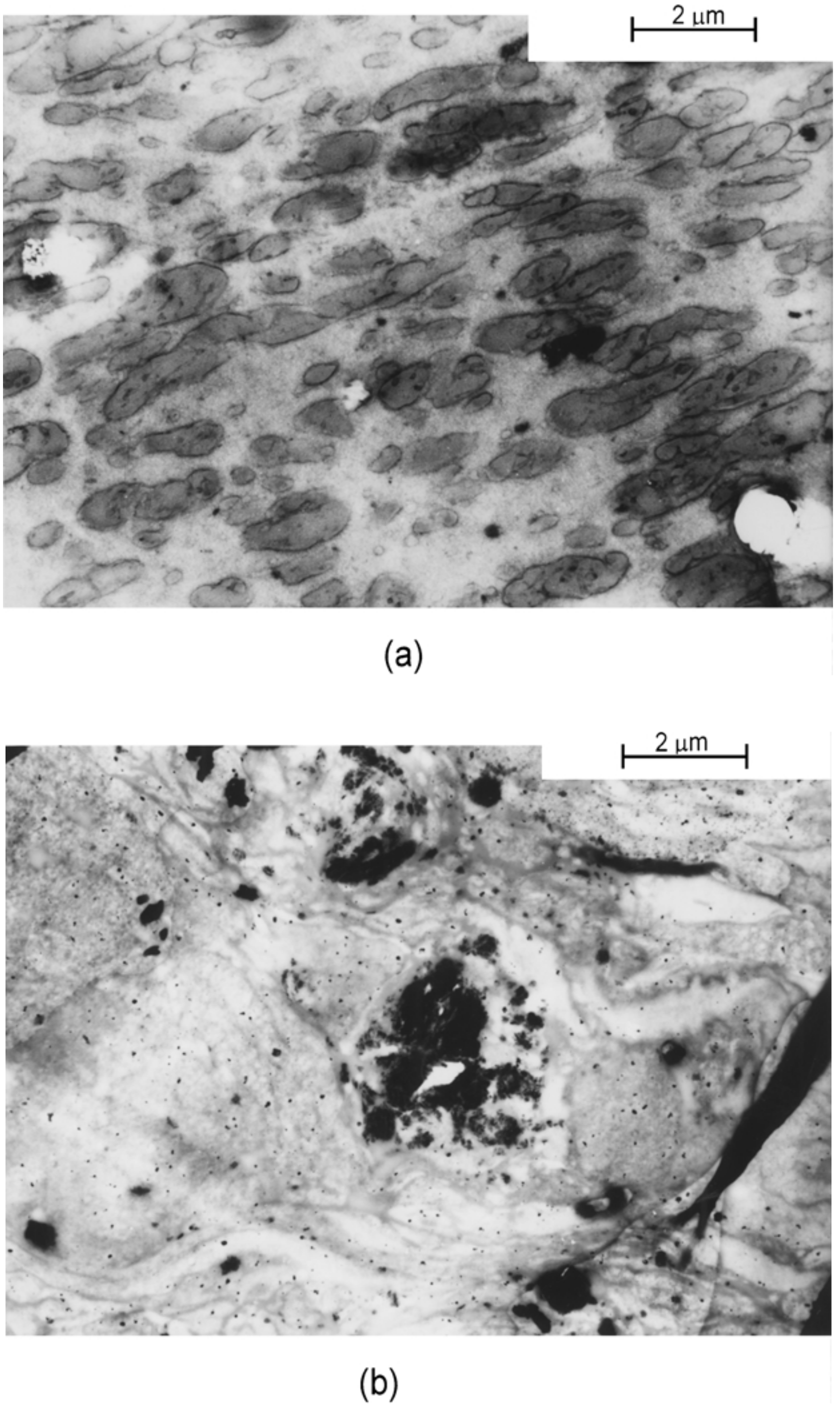


Figure 4 Transmission electron microphotograph of (a) press cured ternary blend of 50/50/30 (w/w) ACM/FKM/pTMPTA and (b) dynamically vulcanized 50/50/30 (w/w) ACM/FKM/pTMPTA blend.

morphology is just one factor influencing properties; other factors like crosslink density, structure of the acrylate etc. play an equal role in controlling the mechanical properties.

3.3. Effect of vulcanisation

Fig. 4a shows the TEM micrograph of press cured ternary blend of 50/50/30 ACM/FKM/p-TMPTA. On comparison with uncured homologue, this blend does not show much variation excepting the change in particle size and its distribution. In addition, the added vulcanising ingredients ($Ca(OH)_2$, MgO, etc.) are distributed in both the phases in the form of tiny spots. Curing of FKM and or ACM leads to agglomeration of particles to the level of micrometer size .

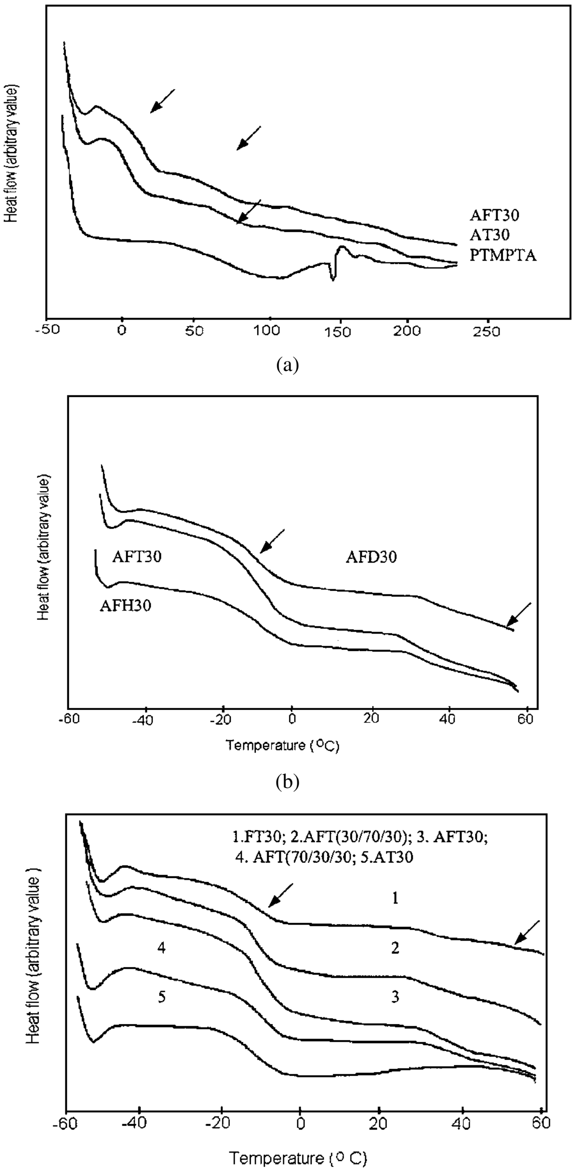
Fig. 4b shows the TEM micrograph respectively of the dynamically vulcanised ternary blend, AFT30. It is understood from the figure that during mixing and subsequent curing in the mixing chamber, there will be preferential curing of the FKM phase by hexamethylenediamine carbamate (DIAK#1) resulting in localised centres of phase separation as seen in the micrograph.

3.4. DSC and DMTA studies

The Differential Scanning Calorimetric (DSC) curves of neat p-TMPTA, AT30 and AFT30 are given in Fig. 5a and Table III. The DSC thermogram of p-TMPTA shows the glass transition (T_g) around 60°C followed by a heat inflection in the temperature range of 150–180°C due to self cross-linking reaction of multifunctional acrylate. The AT30 displays the T_gs of constituent polymers, ACM and p-TMPTA, at -10.6 and 60°C respectively. The absence of heat inflection at higher temperature in this blend may be due to either absence or negligible amount of crosslinking of TMPTA in the presence of ACM. TMPTA undergoes polymerisation and grafting with ACM rather than crosslinking. The same phenomenon is observed with other blends too.

Fig. 5b and c shows the DSC curves of the binary and the ternary blends. Addition of acrylate does not alter the T_g of rubber phase of either ACM, FKM or their blend significantly, which fall in the range of -12 to -9.5°C. There is not much difference in the DSC curves of various acrylates containing blends. It is inferred that the DSC method does not give much insight into the phase morphology in the present case.

The dynamic mechanical spectra of ACM, FKM and AFT30 are represented in Fig. 6. ACM and FKM do not show much variation in their T_gs when added to TMPTA. However, the loss tangent (tan δ) value at T_g is decreased drastically from highest value shown by neat ACM to a lower value given by AT30. The same trend is also observed for FT30 blend. Due to the presence of plastic phase as the continuous matrix, the restriction is imposed on the rubber chain mobility leading to a reduction in the loss tangent at T_g. ACM undergoes interaction with TMPTA through a grafting reaction during mixing resulting in formation of phase structure at the nanoscopic level. FKM, on the other hand, does not show much change in T_g due to the low level of grafting due to difference in chemical nature of the acrylate and the fluorocarbon rubber.



(a) (b) (c)

Figure 5 Differential scanning calorimetry curves of (a) homopolymer of TMPTA and binary & ternary blend of TMPTA with ACM & ACM/FKM; (b) ternary blend of 50/50/30 (w/w) ACM/FKM with various polyacrylates; and (c) blends containing various compositions of ACM and FKM.

TABLE III DSC data of thermoplastic elastomer

Sample ID	T_g(°C)	Heat flow (mW/g)
AT30	-10.6	40.2
AFT(70/30/30)	-9.7	27.9
AFT30	-9.8	62.3
AFT(30/70/30)	-11.7	35.1
FT30	-12.1	31.8
AFH30	-9.5	33.8
AFD30	-9.5	42.7

Addition of TMPTA to ACM/FKM blend does not show any change in transition peak position due to the proximity of the transition temperature. However, an appreciable change is observed in loss tangent values at T_g. The plastic TMPTA, which undergoes

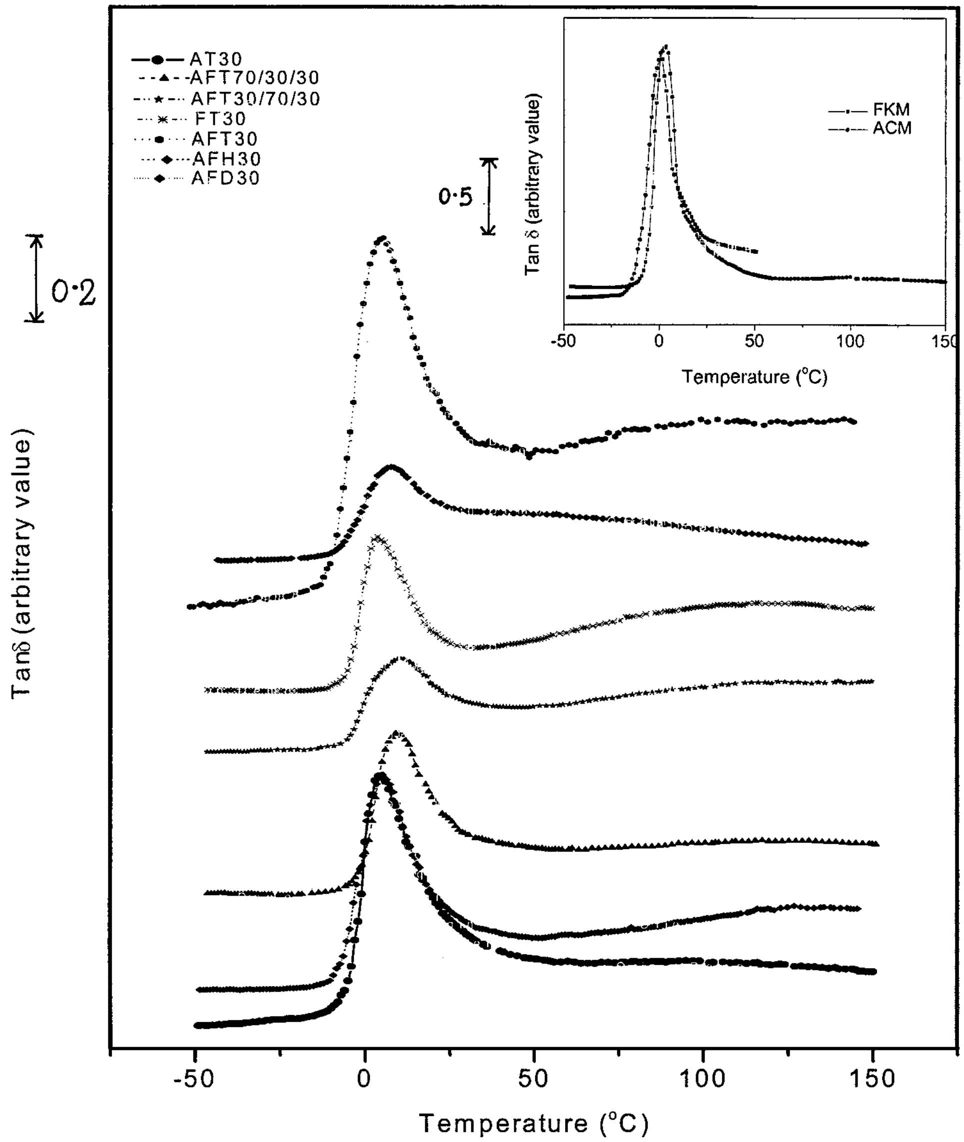


Figure 6 Temperature dependence of tan δ of both binary and ternary blends containing different proportions of ACM & FKM and various polyacrylates.

polymerisation, grafting and cross-linking, restricts the chain mobility of ACM/FKM blend at the transition temperature. Detailed analysis of various spectra has been reported in a separate communication [25].

4. Conclusions

Thermoplastic elastomers developed from blending of multifunctional acrylates with ACM, FKM and ACM/FKM were characterised by Electron Microscopy, Thermal analysis, mechanical testing and dynamic mechanical thermal analysis. The following conclusions were drawn:

1. The miscibility of ACM/FKM is confirmed from TEM studies showing single-phase structure. The binary blend of ACM/p-TMPTA also shows no phase separation between the two polymers indicating compatibility at the nanoscopic level. Upon addition of polyacrylate to ACM/FKM blend leads to phase separation of FKM forming dispersed phase morphology. The size and shape of the dispersed particles are dependent on the concentration of FKM. Polynodal distribution of particles is observed through out the matrix in all blends.

2. The variation of nature of multifunctional acrylates also changes the dispersed phase morphology. Increasing the multi-functionality increases the incompatibility between phases.The processing parameters such as viscosity affects the deformation of particles which in turn is reflected in the elongational properties.

3. The development of microstructure is well correlated with mechanical properties. The overall performance of AFT30 blend compared other blends of different compositions and with different acrylates shows that the AFT30 blend has phase structure with polynodal distribution of particles having size in the range of 250 nm to few μm. The particles are almost deformed ellipsoidal in nature.

4. The DSC data show no major changes in the glass transition temperature of the blends.

5. The DMTA results show a decrease of the peak loss tangent value of the blend with multifunctional acrylates. There is no change in the peak transition

temperature. The tan delta values vary linearly with the multifunctionality of the acrylates.

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