Thermal and Mechanical Properties of Poly(methyl methacrylate) and Ethylene Vinyl Acetate Copolymer Blends

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ABSTRACT: A series of poly(methyl methacrylate) (PMMA) blends have been prepared with different compositions viz., 5, 10, 15, and 20 wt % ethylene vinyl acetate (EVA) copolymer by melt blending method in Haake Rheocord. The effect of different compositions of EVA on the physico-mechanical and thermal properties of PMMA and EVA copolymer blends have been studied. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) has been employed to investigate the phase behavior of PMMA/EVA blends from the point of view of component specific interactions, molecular motions and morphology. The resulting morphologies of the various blends also studied by optical microscope. The DSC analysis indicates the phase separation between the PMMA matrix and EVA domains. The impact strength analysis revealed a substantial increase in impact strength from 19 to 32 J/m. The TGA analysis reveals the reduction in onset of thermal degradation temperature of PMMA with increase in EVA component of the blend. The optical microscope photographs have demonstrated the PMMA/EVA system had a microphase separated structure consisting of dispersed EVA domains within a continuous PMMA matrix. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 684–691, 2007

Key words: poly(methyl methacrylate); ethylene vinyl acetate; differential scanning calorimetry; dynamic mechanical analysis; thermogravimetric analysis; impact resistance

INTRODUCTION

The study of polymer blends has undergone rapid development in recent years and is one of the more advanced domains in modern polymer science. Blend systems, which are composed of existing materials, can be developed at reduced cost in order to suit new market requirements. Because the properties of a blend system vary with the compositions, an existing blend can be easily and quickly modified to meet performance and cost objectives required for new or changing markets. This is manifested by the growing number of research publications.[1–6] The most used industrial process is the incorporation of an elastomeric component,[7] which alters the stress distribution in the matrix and contributes to the control of the crack's propagation and termination. This is carried out by mechanical blending in the melt state with various types of elastomers such as olefinic rubbers based on ethylene and propylene.[7,8] The use of these types of elastomers is very convenient due to the similarity in the chemical compositions, which can help the interfacial interaction and also its competitive price.[9]

The maximum use of blending has been achieved in rubber toughened thermosett and thermoplastics.[10] A small amount of discrete rubber particles in glassy plastics can greatly improve the crack and impact resistance of normally brittle plastics, because the rubbery phase acts as a stress concentrator and craze initiator.[11,12] Polymeric blends consisting of a glassy matrix and a rubber like polymeric dispersed phase are known to exhibit improved impact properties.[13] Unlike the modification of thermosett materials, thermoplastics often require only simple physical blending of a particular elastomeric modifier. Rubber-toughened plastics can be used to produce structural parts, which need high impact strength and crack resistance for many emerging engineering applications. The demand for such material is unfolding in automobile to aerospace industries. The toughness can be introduced either by elastomer introduction during the polymerization or dispersion of a thermoplastic elastomer (TPE) phase during compounding. It is well known fact that the impact strength of glassy polystyrene (PS) improves with the incorporation of elastomers such as polybutadiene rubber.[11–14] Gupta and Purwar[15] reported the miscibility of PP (polypropylene)/SEBS (styrene-*b*-ethylene butylene-*b*-styrene)

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blends. Nando and coworkers[16,17] have studied the blends of ethyl methacrylate (EMA) and polydimethyl siloxane (PDMS). Recently Song and Baker[18] reported that the in situ compatibilization of PS/PE blends. Nando and coworkers[19] was also investigated the *in situ* compatibilization of LDPE/PDMS using EVA copolymer as a compatibilizer.

Poly(methyl methacrylate) (PMMA) is one of the most important acrylic polymers used widely because of its excellent optical clarity and good weathering behavior. PMMA is one of the well known brittle materials and which restricts its applications. In order to enhance the physical and mechanical properties of PMMA, numerous studies have been carried out in the past three decades. The most common method for promoting the toughness of PMMA is blending and copolymerization.

Ethylene vinyl acetate (EVA) elastomer is a suitable material to toughen PMMA because the whole chemical chain of EVA is saturated and elastic. Besides the refractive index of EVA is very close to that of the PMMA and hence the optically clear PMMA blends can possibly be produced. EVA is a copolymer which provides outstanding toughness and resilience and maintains flexibility over broad temperature range. EVA has good clarity, low temperature flexibility, stress crack resistance, and impact strength. The outdoor weatherability is superior to that of LDPE by virtue of their greater flexibility.

The literature survey reveals that the modification of PMMA by *in situ* polymerization,[20] by rubber modification,[21] polyisoprene[22] and with thermoplastic polyurethane (TPU).[23] In this article, the authors report the preparation of PMMA/EVA blends by melt blending with an objective of improving the toughness of PMMA by utilizing EVA as the impact modifier. The weathering resistance of PMMA is not going to be affected by the addition of EVA as elastomer, because the weatherability of EVA is better than the common rubber due to the absence of double bonds.

EXPERIMENTAL

Materials

PMMA (GUJPOL-P, 876G) with MFI of 6 g/10 min, density of 1.19 g/cc and EVA (29% vinyl acetate content, density 0.9493 g/cc), were supplied by Gujarat State Fertilizers Company, India, and Exxon Mobil Chemicals, USA, respectively.

Compounding

The polymers were pre-dried in an air circulating oven at 80°C for 4 h and mixed well before blending. Melt blending of the polymers in different proportions viz., 95/05, 90/10, 85/15, and 80/20 by

wt/wt % of PMMA/EVA was carried out in 17.5 mm diameter twin screw corotating extruder (HAAKE Rheocord 9000, Germany) having L/D ratio 1 : 18 in the temperature range 145–195°C at 80 rpm. The extrudate strands were cut into pellets and used for further study.

Measurements

The blends were analyzed by differential scanning calorimetry (DSC 2010, TA instruments, Newcastle, DE) to determine the PMMA crystalline properties in the temperature range from 50°C to 250°C in nitrogen atmosphere at the heating rate of 10°C/min. The maxima of glass transition and melting endothermic peaks were taken as glass transition temperature (T_g) and melting temperature (T_m), respectively. The melting peak area was used to calculate the enthalpy of fusion and crystallinity. The peak area was measured from the flat baseline on one side and the maximum change in the curved baseline on the other side.

The test specimens were made per ASTM standard specifications in ENGEL-80 tons automatic injection molding machine in the temperature range 200–245°C and injection pressure of 100 bar and the impact strength tests were performed on Izod-Charpy digital Impact tester (ATSFAAR Italy) as per ASTM D 256 A.

The storage modulus of neat PMMA and its blends were studied by dynamic mechanical analysis (DMA). The DMA was carried out using NETZSCH DMA 242 instruments in 3 point bending mode from −150°C to +150°C. The testing frequency was 1 Hz and the heating rate was 5°C/min in air atmosphere.

The TGA thermograms were obtained using TA instrument, TGA 2950 (USA) thermal analyzer at a heating rate of 20°C/min. in a nitrogen atmosphere. The TGA profiles were recorded over a temperature range of 30–800°C. The weight of the samples used for each analysis was 6–8 mg. The surface morphology was on Leica microsystems optical microscope, Leica MeF4, Wetzlar, Germany.

RESULTS AND DISCUSSION

### Differential scanning calorimetric analysis

PMMA and EVA copolymer blends were prepared by melt blending method containing 0, 5, 10, 15, and 20 wt % of EVA. The thermal properties of these blend samples were investigated by (DSC) technique to analyze the effect of EVA content on glass transition temperature (T_g), melting temperature (T_m), heat of fusion, and cystallinity.

Glass-transition temperature

The DSC thermograms of PMMA/EVA blends were shown in Figure 1. Where pure PMMA has a single glass transition temperature (T_g) at 100.6°C. The T_g was used to describe polymer chain segments motion. The EVA copolymer has a single T_g at −26.9°C and a double melting peaks at 47.9 and 70.8°C respectively. However, the PMMA/EVA blends show two glass transition temperatures and a double melting peak corresponding to EVA melting in between the T_gs in all the compositions in the interval of the temperature studied (−150°C to +150°C). The presence of two T_g's shows the heterogeneous nature and immiscibility of EVA in PMMA. The miscibility of the blend is usually determined by the glass transition behavior. Miscible blends show single T_g with shift or broadening, whereas the two phase blends on the other hand show two T_gs characteristics of each phase, when two T_gs are observed, they are not identical those of pure polymers. Further with increase of EVA content, the T_gs of the individual polymer shows outward shift due to increase in incompatibility. The T_g corresponding the PMMA component increase from 107.8°C to 110.8°C and the T_g corresponding to the EVA decreased from 24.1°C to 08.7°C. Comparing the structure of PMMA and EVA, we note that the carbonyl group in the EVA is linked to the main chain carbon atom through an —O— bridge and thus it is easier for it to approach another component to form associations. In PMMA, however, the carbonyl is directly connected to the carbon atom of the main chain and is hence less accessible to the portions of another component. This may be one of the main reasons for the poor miscibility of PMMA with EVA.

Melting temperature and crystallinity

The most important factor that determines whether a polymer can crystallize or not is its geometrical structure, i.e., the configuration of the chain. Stereoregular isotactic and syndiotactic polymers are found to crystallize, EVA exhibits a double melting peak at 47.9°C and another one at 70.8°C. What was observed was a crystalline-Phase separated system that exhib-
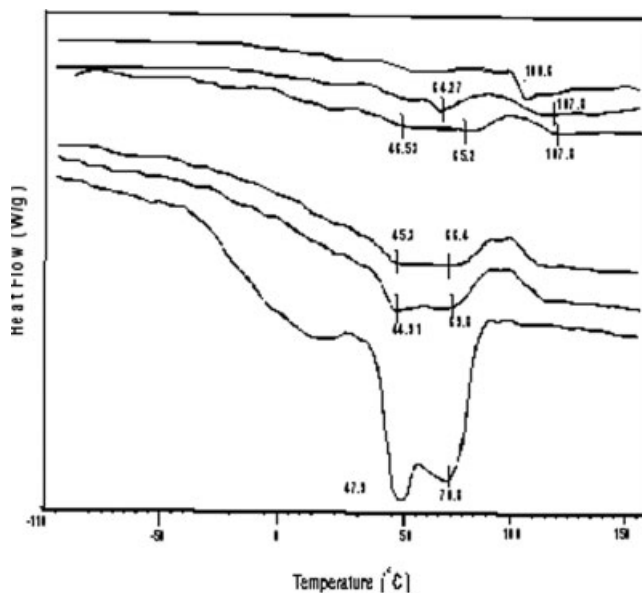
Figure 1 DSC thermograms of PMMA, EVA and their blends.

ited a dual melting point. That dual melting point arose from two crystal phases: one formed primarily by syndiotactic sequences and the other primarily by atactic/isotactic sequences. The two types of crystals have melting points that differ by about 20–30°C. The study of the degree of crystallinity is very significant to understand the changes in the structural characteristics induced by EVA. Probably the most widely used technique for estimating degree of crystallinity is by heat of fusion measurements from DSC thermograms.

A summary of the thermal properties of these PMMA/EVA blends obtained from DSC is shown in Table I. Table I shows the variation of melting enthalpy (0.47–9.84 J/g) as a function of the composition. Apparently the value of melting enthalpy increases gradually with increase in EVA content, indicating increase in crystallinity. The crystallization temperature (T_c) of blends decreased from 50.1 to 37.7 for the addition of EVA content from 5 to 20 wt %. It is well known fact that the crystallinity of the EVA copolymer is provided by the polyethylene sequence of the backbone.

TABLE I
**Data Obtained from DSC Thermograms of PMMA/EVA Blends**

Sample	T_{g1} (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{g2} (°C)	ΔH (J/g)
PMMA 100	–	–	–	–	100.6	–
PMMA95/EVA05	24.1	50.1	–	64.3	107.8	0.47
PMMA90/EVA10	14.9	35.1	46.5	65.2	107.8	3.25
PMMA85/EVA15	11.7	36.1	45.3	66.4	109.5	7.71
PMMA80/EVA20	08.7	37.7	44.9	69.8	110.8	9.84
EVA 100	−26.9	36.7	47.9	70.8	–	38.3

Impact strength

The impact strength evaluation is an important tool to study the toughening effect of rubber in modified plastics. The influence of EVA incorporation on the impact strength of blends is shown in Figure 4. PMMA is a brittle material and have notched impact strength of 19.1 J/m. The incorporation of EVA elastomer into PMMA from 5% to 20% enhances the impact strength of PMMA from 19.1 to 31.96 J/m. The impact strength of blends was higher than that of virgin PMMA. The impact strength increased with increase in EVA content almost linearly. The impact strength of 20% EVA blend was 31.96 J/m, which is approximately 1.5 times higher than that of virgin PMMA. The improvement in impact strength when an elastomer is added to a polymeric matrix normally implies reduction in stiffness and increase in yield strain. A balance between toughness and stiffness is always required for optimum performance of the toughened polymer.

Dynamic mechanical properties

The investigation of dynamic modulus and damping over a temperature range has proved to be very useful in studying the structure of the polymers and the variation of properties in relation to performance.[24–28] The dynamic modulus indicates the inherent stiffness of material under dynamic loading conditions. The mechanical damping indicates the amount of energy dissipated as heat during the deformation of the material. The dynamic mechanical properties of polymers are usually studied over a wide temperature range ($-150°C$ to $+150°C$). In the region where the dynamic modulus-temperature curve has an inflection point, tan δ curve goes through a maximum. This dissipation is called as T_g region. A few polymeric mixtures are compatible and form one phase systems. However, most mixtures of polymers form two phases due to incompatibility of the components. The modulus and temperatures curves of pure PMMA matrix and its blends containing 5, 10, 15, and 20% of the EVA polymer have been shown in Figure 2. The break in modulus curves remain steep, and the modulus is just shifted on temperature scale in proportion to the relative concentration of two polymers. Now the break in modulus of the curves near T_g is not so steep. The two steps in the dynamic modulus-temperature curves are characteristics of an immiscible two-phase system.[28] Here the DMA analysis has been studied to trace the temperature dependence of storage modulus upon blending with EVA. For all the blend compositions, the storage modulus can be seen decreasing in the investigated temperature range, indicating the introduction of EVA reduces the storage modulus of PMMA
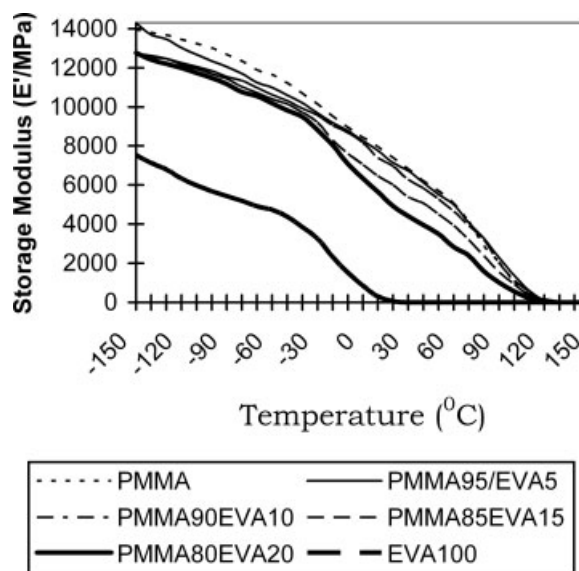
Figure 2 Effect of EVA addition on storage modulus of PMMA blends.

proportionately with the composition. The blends undergo two step reductions in storage modulus, one at the T_g of EVA and the other one at the T_g of PMMA.

With increase in EVA content the reduction of storage modulus at the EVA T_g region is more and vice versa. The modulus of elasticity in the glassy state for the two blends is shown to decrease with increasing EVA content. This result is expected because the material incorporated was a low modulus flexible material.

Dynamic mechanical tests are in many cases the most sensitive tests known for studying glass transition and secondary transition in polymers as well as the morphology of the crystalline polymers. Damping is often the most sensitive indicator of all kind of molecular motions that are going on in a material, even in the solid state. These motions are of great practical importance in determining the mechanical behaviour of polymers. For this reason, the absolute value of damping, its sensitivity to the magnitude of the strain and temperature at which the damping peaks occur are of considerable interest. Many other mechanical properties are intimately related to damping; these include toughness, impact strength and breaking strain. In the transition region, the damping is high owing to the initiation of micro Brownian motion in molecular chains. Some of the molecular chain segments are free to move, others or not. A frozen segment can store much more energy for a given deformation than a free-to-move rubbery segment. Thus every time a stressed, frozen-in segment becomes free to move. Its excess energy is dissipated as heat. Micro-Brownian movement is con-
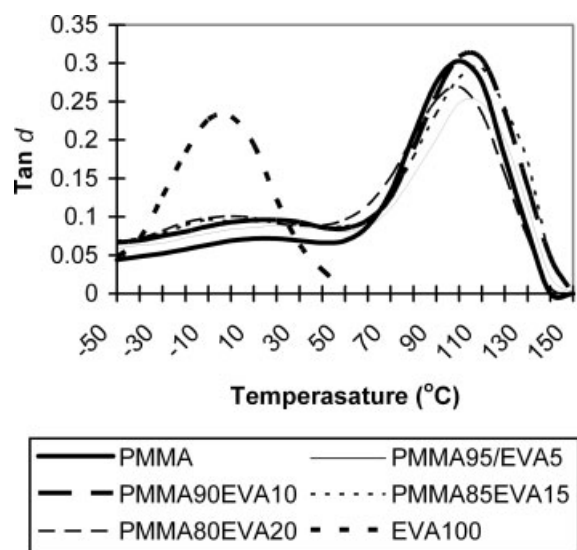
cerned with the cooperative diffusional motion of main chain segments. This transition is so conspicuous that is called the primary dissipation (the α-peak). Other relaxation transitions can be found in a glassy state on the lower temperature side of the primary dispersion. PMMA and other methacrylate esters have very low temperature secondary peaks. In this case the pure PMMA shows a secondary transition at 15.5°C. These are called secondary dispersions and are usually designated as β and associated with side chain motion of the ester group.[29–32] In this case, the damping temperature curve shows two peaks; each peak is characteristic of the T_g of the individual components. Figure 3 shows a typical example. The EVA has maximum dampness at 24.2°C, whereas the PMMA and its EVA blends have dampness at 98.6, 104.1, 104.0, 105.7, and 105.7°C, for 5, 10, 15, and 20% EVA blends, respectively. The magnitude of the peak is more or less characteristic of the relative concentration of the components and whether or not the phases are dispersed or continuous.[33–35] For instance at a given concentration, tan δ is greater in the high temperature damping peak, if the polymer with high T_g value is in continuous phase.[33]

The T_g obtained by DSC and DMA analysis of PMMA/EVA blends are given in Table II. From the Table, it is clear that both method gives similar type of results. In both cases, T_g has broadened with increase in EVA content, indicating reduction in compatibility with increase in EVA content.

Thermogravimetric analysis

TGA studies in terms of weight loss curves of PMMA/EVA blends are shown in Figure 5. EVA

TABLE II
Analysis of Glass Transition Temperature of PMMA/EVA Blends

Sample	DSC analysis		DMA analysis	
	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
PMMA100	–	100.6	–	098.6
PMMA95/EVA05	24.1	107.8	64.3	104.1
PMMA90/EVA10	14.9	107.8	65.2	104.1
PMMA85/EVA15	11.7	109.5	66.4	105.7
PMMA80/EVA20	08.7	110.8	69.8	105.7
EVA100	−26.9	–	70.8	–

decomposes by a two step mechanism; the first step (300–350°C) corresponds to pyrolysis of acetic ester group[36] of the vinyl acetate with elimination of acetic acid, resulting in the formation of polyenes.[37] The second decomposition step involves random chain scission of the remaining material, forming unsaturated vapor series (430°C), such as butene and ethylene.[38] Deacetylation proceeds through β-elimination of the vinyl acetate groups present in the EVA molecules, up to 100 conversion to polyethylene macromolecules, containing polyene sequences having up to four conjugated double bonds. During thermal degradation the polymer crosslinks rapidly, and appears to be autocatalytic. These crosslinking reactions lead to the formation of a protective layer, which limits the access to the oxygen to the remaining material, and impedes the flow of fuel to the gas phase. Figure 6 shows the TGA derivative of pure PMMA, PMMA95/EVA05, and pure EVA. While

Figure 3 Effect of EVA addition on Tan δ of PMMA blends.
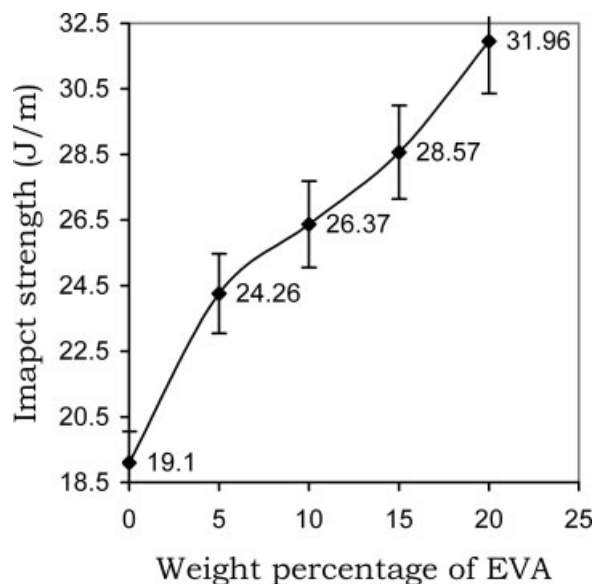
Figure 4 Influence of EVA addition on impact strength of PMMA blends.

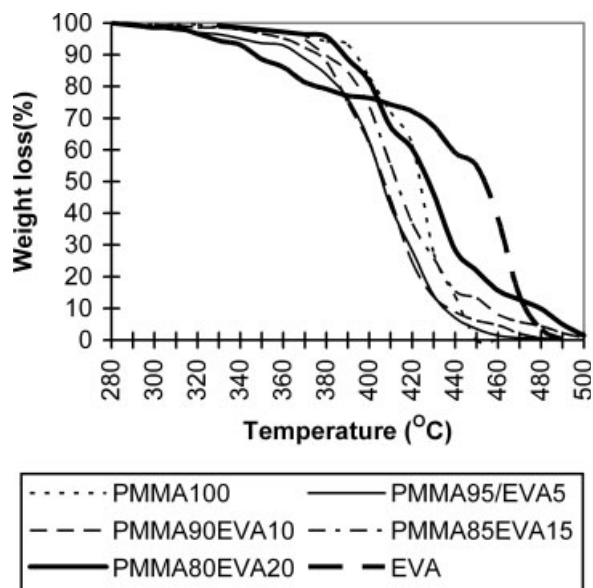**Figure 5** TGA thermograms for PMMA/EVA blends.

Figure 7 TGA derivative graphs of PMMMA/EVA blends.

looking closely at the curves, one can observe that the maximum weight loss for pure PMMA occurs at 430°C and for pure EVA maximum weight loss for the first degradation event occurs at 352°C, its second degradation occurs at 470°C. For the PMMA blend containing 5% of EVA, the first stage degradation is not visible but, the second degradation occurs at 407°C. This brings out two points: one, the second stage degradation (thermal stability) of EVA is better than that of pure PMMA; second, the addition of EVA into the PMMA matrix, reduces the thermal
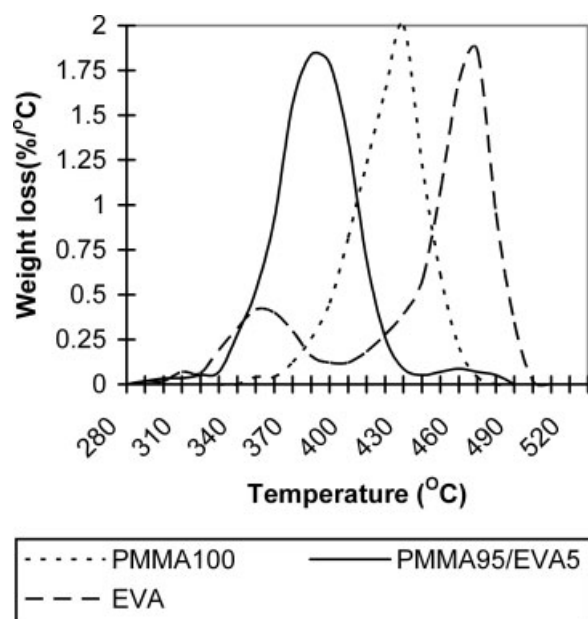
stability of PMMA significantly. Figure 7 shows the TGA derivative curves of PMMA blends containing 5, 10, 15, and 20 wt % of EVA, which again shows two stage degradation, the first stages peak maxima of these blends are between the peak maxima of pure PMMA (430°C) and pure EVA (470°C as seen in Figure 6.

Surface morphology

The surface morphology of the system strongly influences the properties of polymer blend.[39] The optical micrographs of PMMA and EVA are given in Figure 8(a,b) respectively. These figures show two phase morphology for PMMA as well as EVA. The two phase morphology of PMMA is due to the existence of amorphous and crystalline phase. The two phase morphology in case of EVA is due to the presence of ethylene and vinyl acetate groups. The photo micrographs of the blends shown in figures [Fig. 8(c–f)] clearly indicate changed surface morphology of blends compared with that of pure polymers although the boundary region of the phases are not very sharp. At higher level of EVA incorporation (20%) somewhat irregularity in structure appears to develop, which leads to increase in impact strength. Comparing the structures of PMMA and EVA, we note that the carbonyl group in EVA is linked to the main-chain carbon atom through an —O— bridge and thus it is easier for it to approach another component to form associations. In contrast, in PMMA, the carbonyl group is directly connected to the carbon atom of the main-chain and is hence less accessible to the protons of

Figure 6 TGA derivative graphs of PMMA/EVA blends.
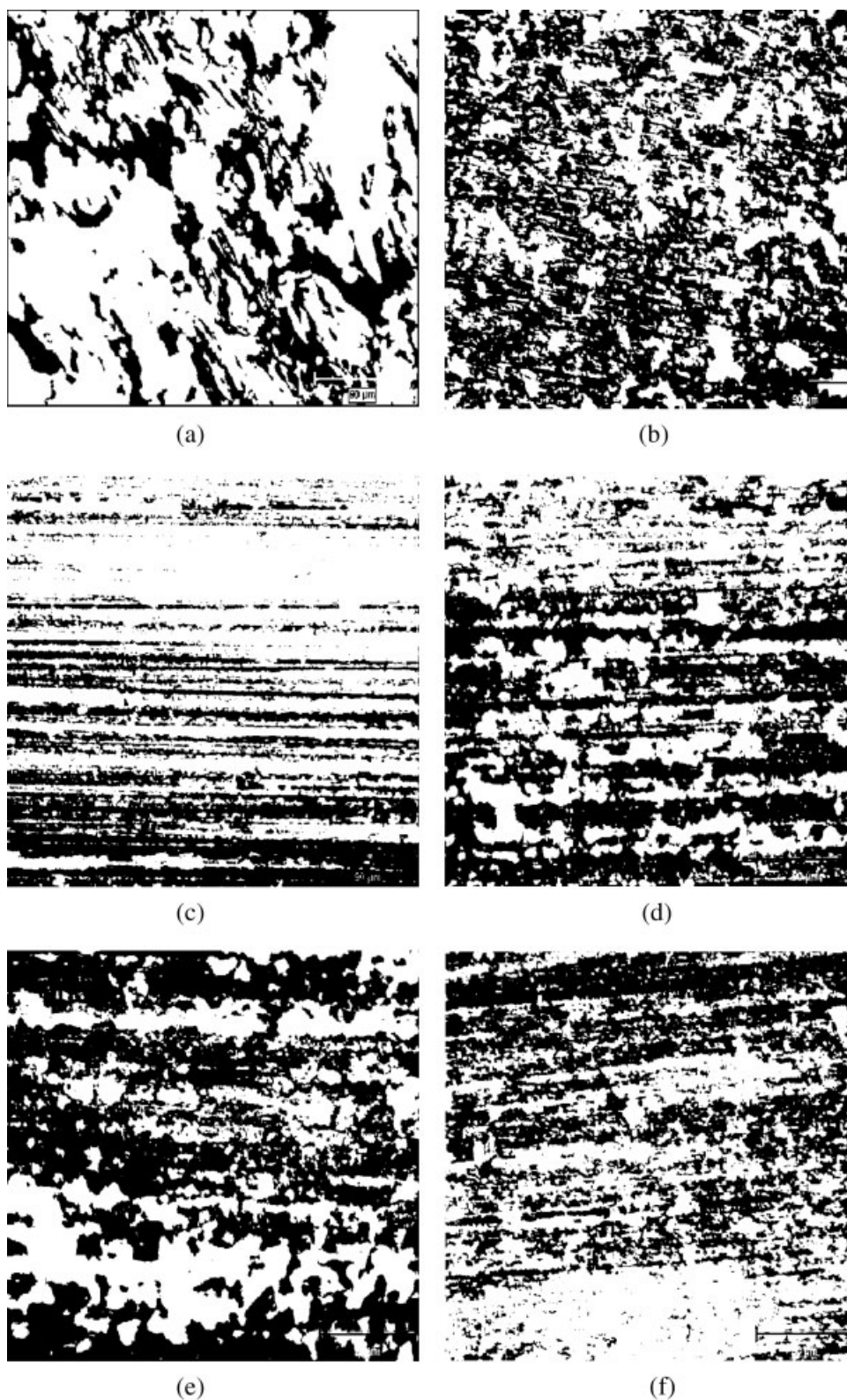
Figure 8 (a) PMMA100, (b) EVA100, (c) PMMA95/EVA05, (d) PMMA90/EVA10, (e) PMMA85/EVA15, (f) PMMA80/EVA20.

another component. This may be one of the main reasons for the poor compatibility of PMMA and EVA.

CONCLUSIONS

This study examines the phase behavior of PMMA and EVA copolymer blends. DSC and DMA analysis

shows the two T_gs indicating two phase morphology and incompatibility in PMMA/EVA blends and compatibility reduces with increase in EVA component. The impact strength analysis revealed a substantial increase in impact strength from 19 to 32 J/m. The various polyblends exhibit two stage thermal degradation typical of EVA and all of blends show reduction in thermal stability in terms of onset of degradation after incorporation of EVA into PMMA matrix. The optical microscope photographs have demonstrated the PMMA/EVA system had a microphase separated structure consisting of EVA domains within a continuous PMMA matrix.

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