Poly(Methyl Methacrylate) Toughened by Ethylene-Vinyl Acetate Copolymer: Physico-Mechanical, Thermal, and Chemical Properties

P. Poomalai,[1] B. Ramaraj,[1] Siddaramaiah[2]

[1]*Central Institute of Plastics Engineering and Technology (CIPET), 437/A, Hebbal Industrial Area, Mysore 570016*
[2]*Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, Mysore 570016*

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ABSTRACT: Blends of poly(methyl methacrylate) (PMMA) with different composition viz., 5, 10, 15, and 20 wt % of ethylene-vinyl acetate (EVA) copolymer were prepared by extrusion in a corotating twin screw extruder. These prepared PMMA/EVA blends have been characterized for physicomechanical properties such as density, surface hardness, izod impact strength, tensile strength, tensile elongation, and tensile modulus. The chemical aging and heat aging tests were performed on the blends by exposing them to different chemical environments and to 80°C for 168 h respectively. The influence of chemical aging and heat ageing on the mechanical performance of PMMA/EVA blends has been studied. The PMMA/EVA blends were also characterized for thermal properties such as vicat softening point (VSP) and melt flow index (MFI). That means significant improvement in impact strength of PMMA was noticed after incorporation of EVA into PMMA matrix and it lies in the range 19.1–31.96 J/m. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3145–3150, 2007

Key words: impact resistance; chemical ageing; tensile properties; poly(methyl methacrylate); ethylene-vinyl acetate

INTRODUCTION

During the past decades remarkable advances have been made both scientifically and technologically in the area of polymer blends. Owing to strong economic incentives, modification of existing materials by blending is becoming one of the attractive route to improve properties and to generate versatile polymeric products. 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 in 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 elastmers 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 are often require only the simple physical blending of a particular elastomeric modifier. Rubber toughened plastics can be used to produce structural parts, which needs high impact strength and crack resistance for many emerging engineering applications. The demand for such material is unfolding from 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 a well known fact that the impact strength of glassy polystyrene (PS) improves with the incorporation of elastomers such as polybutadiene rubber.[11–14] Gupta et al.[15] reported the miscibility of PP (polypropylene)/SEBS (styrene-*b*-ethylene butylene-*b*-styrene) blends. Nando et al.[16,17] have studied the blends of EMA/PDMS. Recently Song and Baker[18] reported the *in situ* compatibilization of PS/PE blends. Nando et al.[19] was also investigated the *in situ* compatibilization of LDPE/PDMS using EVA copolymer as a compatibilizer.

Correspondence to: Siddaramaiah (siddaramaiah@yahoo.com).

Poly(methyl methacrylate) (PMMA) is one of the most important acrylic polymers used widely because of its excellent clarity and good weathering behavior. It is hard, stiff, and brittle thermoplastic at room temperature. However, it has poor impact and solvent resistance, which restrict its applications. Ethylene-vinyl acetate (EVA) has been investigated as impact modifier and can be used as toughening agent in brittle and notch sensitive polymer because they behave either as dispersed rubber phase or dissolved in them. EVA is a copolymer that provides outstanding toughness and resilience and maintain flexibility over broad temperature range. EVA has improved clarity, low temperature flexibility, stress crack resistance, and impact strength. The out door 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. The refractive index of the PMMA and EVA are also close to each other at ambient temperature.

EXPERIMENTAL

Materials

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

Compounding

The polymers were predried 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 percentage of PMMA/EVA was carried out in 17.5 mm dia 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 test specimens were made as 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. The impact strength tests were performed on Izod-charpy digital Impact tester (ATSFAAR Italy) as per ASTM D 256 A. The tensile tests were carried out on injection molded dumb-bell specimens in Universal testing machine (Llyod, UK, Model LR 100K) as per ASTM D638 standard with cross-head speed of 50 mm/min. Chemical resistance test was carried out as per ASTM D 543 by immersing the tensile specimens in different chemical reagents (aqueous solutions of acids and alkali) for 168 h. Heat ageing test was carried out as per ASTM D 794 by suspending the tensile specimens in the air circulating oven at 80°C for 168 h. The density of the blends was measured as per ATSM D 792. Melt flow index (MFI) testing was performed on extrudate cut pellets in melt flow index tester (Devanport, UK, Type 7273) at 230°C and 1.2 kg load as per ASTM D 1238. Vicat softening point (VSP) measurements were made as per ASTM D 1525 test method in HDT-VICAT Tester (ATS FAAR, Italy, model MP/3). Shore D hardness was measured using Durometer (M/s. P.S.I Sales Pvt. Ltd., India) as per ASTM D 2240 test method.

RESULTS AND DISCUSSION

Physicomechanical properties

The measured properties such as density, surface hardness, melt flow index (MFI), vicat softening point (VSP), and tensile behavior of PMMA/EVA blends are given in Table I. We also calculated the

TABLE I
Physico-mechanical properties of PMMA/EVA blends

Composition of PMMA/EVA weight (%)	Density, Kg/m^3 (±1.2%)	Tensile strength, MPa (±5.0%)	Tensile modulus, MPa (±6.6%)	Tensile elongation, % (±6.0%)	Surface hardness, Shore D (±5.0%)	Melt flow index, 230°C/3.8 kg (g/10 min)	Vicat softening point (°C)
100/00	1183	78.54	1213	11.0	90	4.33	95.0
95/05	1162	62.85	503	19.0	88	16.71	94.4
90/10	1148	40.89	394	12.8	84	19.28	93.4
85/15	1138	34.42	324	12.3	79	23.75	92.3
80/20	1124	26.38	249	11.6	77	26.13	91.5

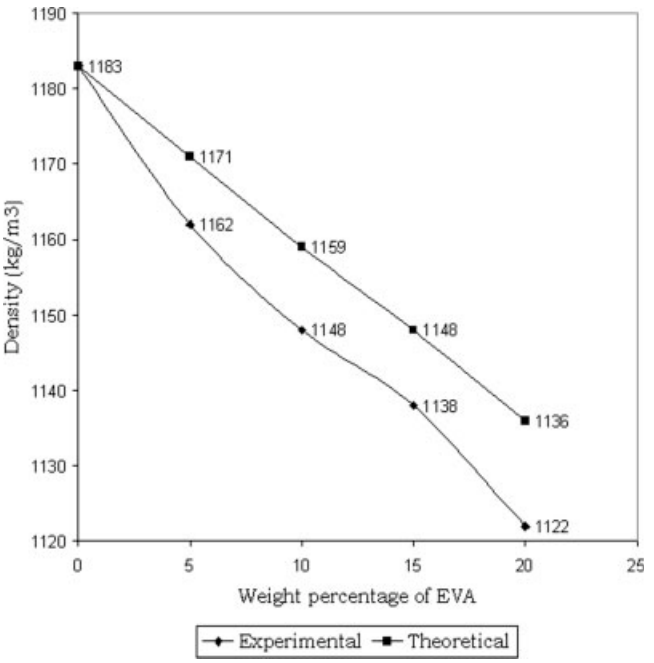

Figure 1 Influence of EVA addition on density of PMMA/EVA blends.

densities by volume additive method, which states that ($d = w_1d_1 + w_2d_2$), where d is the density of the blend, w_1 and w_2 are the weight fractions of the constituents, and d_1 and d_2 are the corresponding densities. The plot of density versus EVA composition for the PMMA/EVA blends are shown in Figure 1, which shows density of blends decreased linearly with increase in EVA content. Further actual density values of these blends are lesser than that of its theoretical values calculated by volume additivity principle. The reduction in density may be due to the incompatibility and micro void formation, poor interfacial adhesion, or phase separation between PMMA and EVA, which is well supported by increase in impact values of PMMA/EVA blends with increase in EVA content.

The melt flow index (MFI) values shows increases from 4.33 to 26.13 g/10 min as the percentage of EVA increases in the blend composition (Table I). This increase in MFI may be due to incompatibility between PMMA and EVA, low molecular weight of EVA, and reduction in softening temperature of the blend after incorporation of elastomeric EVA phase. From MFI value it can be concluded that the behavior of processability of the blend enhanced when compared with PMMA.

The VSP is one of the methods to assess the elevated temperature performance of plastics. From the Table I it was noticed that the VSP of virgin PMMA is 95°C, decreased gradually with the addition of EVA. At 20% EVA, the VSP of the blend is 91.5°C. This result clearly indicates a slight reduction or retain in VSP value upto 20% in the blends. This is in accordance with the theoretical expectations, because of the low VSP value, 42°C of EVA.

The surface hardness values for virgin PMMA and its blends (Table I) indicate decrease in hardness with increase in EVA content. The surface hardness value of the blend lies in the range 77–88 Shore D, while that of PMMA was 90 Shore D. This as expected because of the increase in EVA content in thermoplastic phase and its incompatibility with PMMA.

Impact strength

The impact strength evaluation is an important tool to study the toughening effect of rubber in modified plastics. The influence of EVA addition on the impact strength of blends is shown in Figure 2. 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 approximately one and half 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 increases in yield strain. A balance between toughness and stiffness is always required for optimum performance of the toughened polymer.

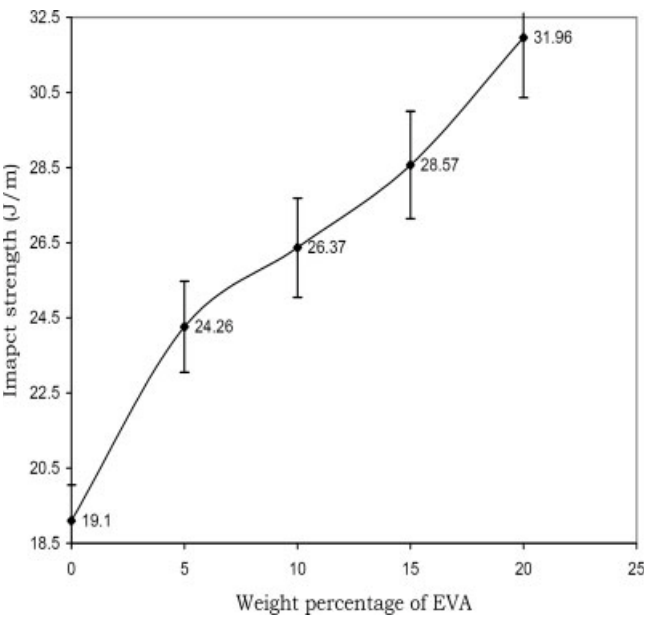

Figure 2 Influence of EVA addition on impact strength of PMMA/EVA blends.

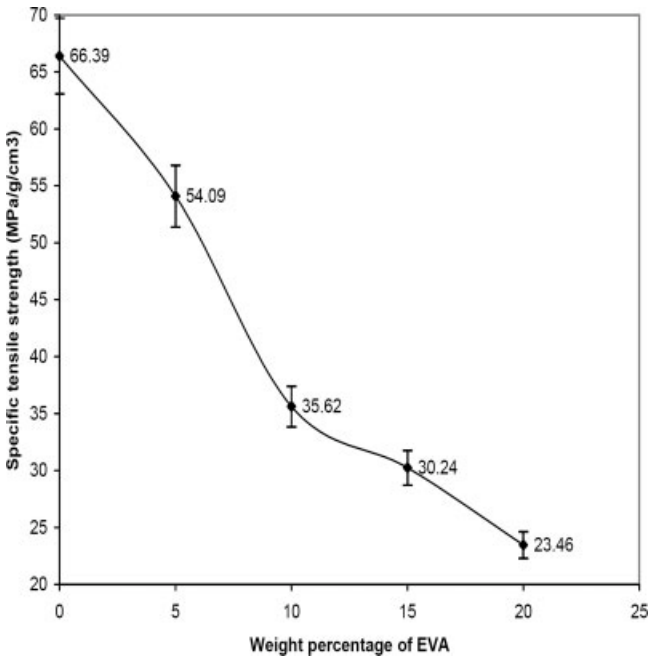

Figure 3 Influence of EVA addition on tensile strength of PMMA/EVA blends.

Tensile behavior

The effect of EVA composition on specific tensile strength of PMMA/EVA blends is shown in Figure 3. From Table I it is noticed that the tensile strength and tensile modulus decreases drastically with the EVA loading. The tensile strength decreased from 78.54 to 26.38 MPa, whereas the tensile modulus decreased from 1213 to 249 MPa. The addition of elastomer into a brittle polymer normally implies reduction in maximum load at yield and stiffness. In case of tensile elongation, even though there is an increase for the addition of 5% EVA, however further addition does not change tensile elongation significantly.

TABLE III
Influence of chemical ageing on tensile elongation of PMMA/EVA blends

	Tensile strength, MPa (±5.0%), for EVA (wt %) in blend				
Chemical resistance	0	5	10	15	20
Before ageing	11.00	19.00	12.8	12.30	11.60
In alkali					
5% Na_2CO_3	10.47	11.95	7.70	8.26	7.62
5% NaOH	13.66	11.78	7.87	8.23	7.43
5% NH_4OH	10.91	12.04	6.85	7.53	7.95
In acids					
5% CH_3COOH	10.67	10.60	8.27	7.95	8.01
5% HCl	11.60	10.82	7.97	7.85	7.70
5% H_2SO_4	13.49	11.09	7.69	8.45	7.14
In water	12.76	10.98	7.31	8.34	8.02

Effect of chemical ageing

The method of measuring the resistance of plastics to chemical reagents by simple immersion of plastic specimen is a standard procedure used throughout the plastic industry. This method can be used to compare the relative resistance of various plastics to typical chemical reagents. The specimens are totally immersed in different chemical reagents for seven days in a standard laboratory atmosphere. After seven days the specimens were removed from the reagents and performed for tensile properties. The tensile strength results of PMMA and its blends before and after chemical ageing in different chemical environments are given in Table II. Which shows the tensile strength of virgin PMMA after ageing declined about 4–20%. Whereas in case of blends the reduction in tensile strength is lies in the range 0.28–7.7%. These results reflected the enhancement of chemical resistance after blending.

Table III presents the tensile elongation results of PMMA and its blends before and after chemical age-

TABLE II
Influence of chemical ageing on tensile strength of PMMA/EVA blends

	Tensile strength, MPa (±5.0%), for EVA (wt %) in blend				
Chemical resistance	0	5	10	15	20
Before ageing	78.54	62.86	40.89	34.42	27.06
In alkali					
5% Na_2CO_3	62.56	62.27	39.42	34.03	26.67
5% NaOH	75.41	62.17	40.20	33.44	26.97
5% NH_4OH	76.58	62.36	40.59	34.32	26.87
In acids					
5% CH_3COOH	73.74	58.35	38.24	31.87	25.79
5% HCl	75.02	62.66	38.53	33.44	26.57
5% H_2SO_4	75.70	62.27	40.59	34.32	24.61
In water	72.07	62.07	39.32	34.22	26.87

TABLE IV
Influence of chemical ageing on tensile modulus of PMMA/EVA blends

	Tensile strength, MPa (±6.6%), for EVA (wt %) in blend				
Chemical resistance	0	5	10	15	20
Before ageing	1213	503	394	324	249
In alkali					
5% Na_2CO_3	933	778	612	502	387
5% NaOH	1161	770	652	511	389
5% NH_4OH	1123	872	563	613	379
In acids					
5% CH_3COOH	1084	745	699	630	500
5% HCl	1151	946	711	683	483
5% H_2SO_4	1127	796	735	579	475
In water	1091	927	561	625	399

TABLE V
Influence of heat ageing on tensile properties of PMMA/EVA blends

PMMA/EVA Composition (wt/wt %)	Tensile strength, MPa (±5.0%)		Tensile elongation, %, (±6.0%)		Tensile modulus, MPa, (±6.6%)	
	Before ageing	After ageing	Before ageing	After ageing	Before ageing	After ageing
100/00	78.6	64.6	11.0	6.7	1213	962
95/05	62.9	61.0	19.0	8.8	503	827
90/10	40.9	29.8	12.3	4.6	394	684
85/15	34.4	28.4	11.6	4.8	324	576
80/20	36.2	23.3	12.8	5.9	249	457

ing. The percentage tensile elongation of virgin PMMA retains the properties after chemical ageing, but for the blends, the percentage tensile elongation is found to be reduced in all blend compositions after ageing. The measured tensile modulus results of PMMA and its blends before and after chemical ageing is given in Table IV. A slight reduction or retained in tensile modulus of PMMA was noticed after chemical aging. But in case of PMMA/EVA blends, the tensile modulus has decreased for all the blend compositions and for all chemical reagents. The tensile behavior results after chemical ageing indicates that the enhanced stiffness and resistance to deformation after chemical ageing.

Chemical resistance is a complex subject. Plastics resistance to chemicals is best understood through study of its basic polymer structure. The type of bonds, the degree of crystallinity, branching, the distance between the bonds, and the energy required to break the bonds are the most important factors to consider while studying the chemical resistance of plastic materials. PMMA is a polar material and will absorb water molecules which affects the mechanical properties, but it is not so in case of blends. The introduction of EVA introduces crystallization, reduces number of side chains and presence of greater intermolecular forces helps the blends to be rigid and resist deformation.

Effect of heat ageing

Plastic materials exposed to heat may be subjected to many types of physical and chemical changes. The severity of the exposures in both time and temperature determines the extent and type of changes that take place. Extended periods of exposure of plastics to elevated temperatures will generally cause some degradation with progressive changes in physical properties. Table V presents the tensile strength, tensile elongation and tensile modulus results of PMMA and its blends before and after heat ageing at 80°C for 168 h. Because of heat ageing, the tensile strength and tensile elongation results decreased, but the tensile modulus of the blends increased, which again indicates the material deterioration with enhancement of stiffness and resistance to deformation after heat ageing. Heat ageing generally relieve mold stress, some plastics become brittle, mechanical properties are sensitive to heat degradation. Polymers such as PMMA and EVA are susceptible to degradation because of the influence of humidity in long term heat resistance test. Material susceptible to hydrolysis may undergo degradation when subjected to long term heat aging test. The tensile strength of both PMMA and its blends decreased because of sensitivity of these materials towards heat and undergoes hydrolytic degradation.

CONCLUSIONS

The toughened poly(methyl methacrylate)/ethylene-vinyl acetate (EVA) copolymer blends were prepared with different compositions viz., 100/0, 95/5, 90/10, 85/15, and 80/20. The prepared PMMA/EVA blends show significant improvement in impact strength and chemical resistance. The impact strength of PMMA increased from 19.1 to 31.96 J/m after incorporation of 20% EVA.

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