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Thermogravimetric studies on miscible blends of ethylene–methyl acrylate copolymer (EMA) and polydimethylsiloxane rubber (PDMS)

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Abstract

Thermogravimetric and derivative thermogravimetric analysis of blends of ethylene–methyl acrylate copolymer and polydimethylsiloxane of different compositions have been investigated. Curves of weight loss and derivative weight loss against temperature show that degradation takes place in two steps with peak maxima, at $T_{1\max}$ and $T_{2\max}$, both proportional to the components in the blends. Kinetic studies show that the degradation of the blends and that of the single components follow first order reaction kinetics. Activation energies of the degradation have been determined using Freeman and Carroll's method and the thermal stability of the blends has been investigated.

INTRODUCTION

The thermal stabilities of polymers, blends and alloys have been reported by several authors [1–4], and Varughese [5] has reported the thermal decomposition and flammability of miscible blends of polyvinylchloride and epoxidized natural rubber. The blending of PVC with other polymers has been reported as having a marked effect on its thermal stability [6].

Silicone rubber has long been recognized as the rubber of choice for high and low temperature service use, and silicone elastomers have been widely adopted in a range of applications [7]. Many blends of polydimethylsiloxane (PDMS) rubber with a range of polymers have been used which satisfy the high degree of performance required under severe service conditions.

No work has been reported on polymer blends of polydimethylsiloxane rubber and ethylene–methyl acrylate copolymer (EMA). Recently, the authors have shown that EMA and PDMS rubber are miscible throughout the composition range, and have suggested a reason for this solubility [8]. PDMS rubber, by virtue of its molecular architecture, has excellent low-

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and high-temperature retention of mechanical properties, excellent ageing and dielectric properties, and excellent thermal stability. However, it imparts poor oil and solvent resistance, inferior mechanical properties and lower surface energy to blends. Above all, its high material cost has restricted its use in many industrial applications.

In the present investigation, EMA has been chosen for its excellent solvent and oil resistance, in particular acid and alkali resistance, and excellent environmental stress cracking resistance at elevated temperature, as well as superior mechanical properties. Furthermore, it has the advantage of a polar ester group and a reactive α-hydrogen atom which can take part in reaction with PDMS. This paper deals with the thermogravimetric analysis of blends of EMA and PDMS rubber with an emphasis on the thermal stability of the blends.

EXPERIMENTAL

Materials

A PDMS rubber containing a small percentage of vinyl group (Silastic WC-50) was supplied by Dow Corning Inc., USA. It had the following specification: specific gravity 1.15, brittle point −39°C.

EMA (OPTEMA TC-120) was supplied by Exxon Chemicals Inc., USA. It had the following specification: methyl acrylate content 21%; melting point 81°C; melt flow index 6.0 dg mm^{-1}; density 0.94 g cm^{-3}.

Preparation of the blend

Mixing of the individual components of the blends was carried out in a Brabender Plasticorder (PLE-330) at 180°C for 10 minutes at 100 rpm. The molten mass was rolled into a sheet using a two roll laboratory mill (150 mm × 300 mm). The sheet was mixed further in the Plasticorder at 130°C, and an optimum amount of dicumyl peroxide (DCP 99%) was added. Mixing was continued for 2 min to obtain a homogeneous mixture. The molten mass was milled to a sheet with the roll mill. The sheet was vulcanized in a compression moulding press at 180°C under 4.5 MPa for the optimum cure time as determined by a Monsanto rheometer model R-100. The optimum dose of DCP was 1.5 phr (parts per hundred parts of rubber) in all cases.

Thermogravimetric studies

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out on a Stanton Redcroft thermogravimetric analyzer model STA 625 equipped with a computer data analyzer version C4.20 in a nitrogen atmosphere at a heating rate of 10°C min^{-1}. The weight of sample used was 5 mg in all cases.

RESULTS AND DISCUSSION

Thermogravimetry and derivative thermogravimetry curves of the blend components are shown in Figs. 1 and 2, and those of the blends are shown in

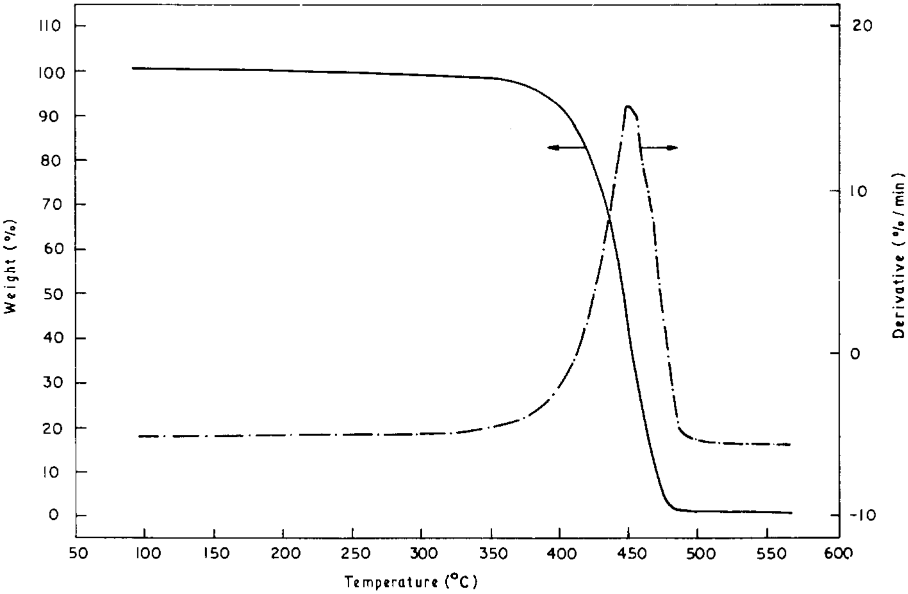

Fig. 1. TGA (——) and DTG (—·—·) curves of ethylene–methyl acrylate (EMA).

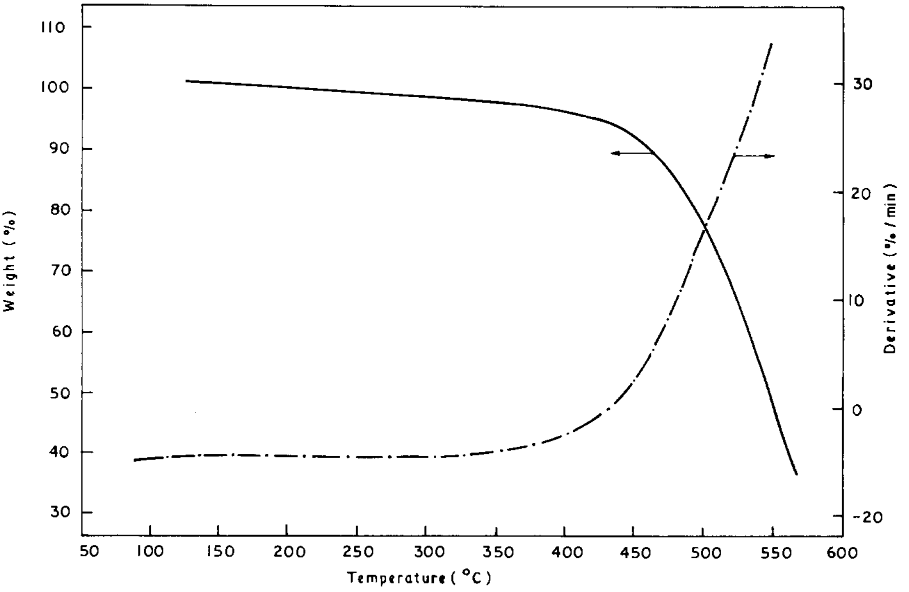

Fig. 2. TGA and DTG curves of polydimethylsiloxane (PDMS).

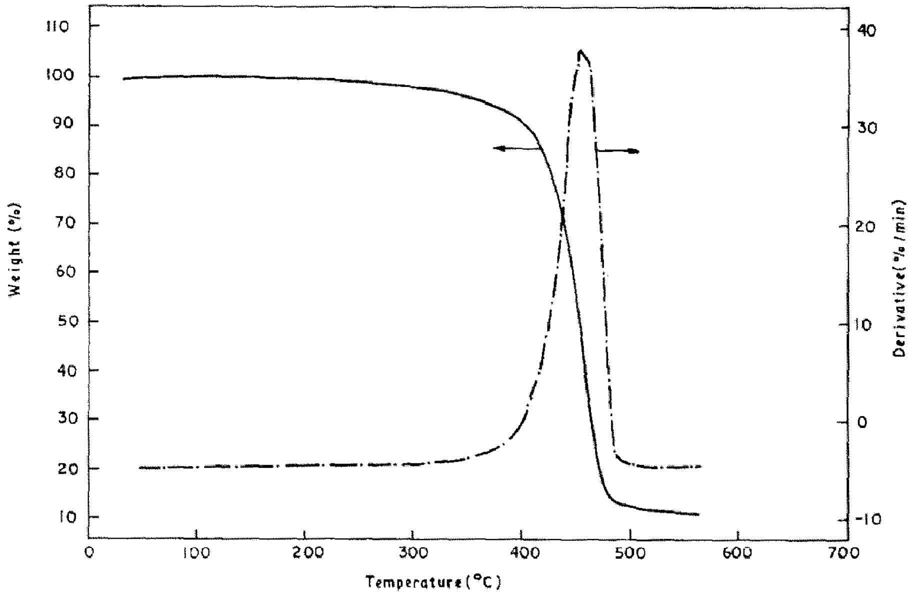

Fig. 3. TGA and DTG curves of 70:30 EMA:PDMS blend.

Figs. 3–5. The thermograms of EMA and PDMS and that of the 70:30 EMA:PDMS blend show only one step degradation, whereas 50:50 and 30:70 EMA:PDMS blends show two step degradation thermograms. The

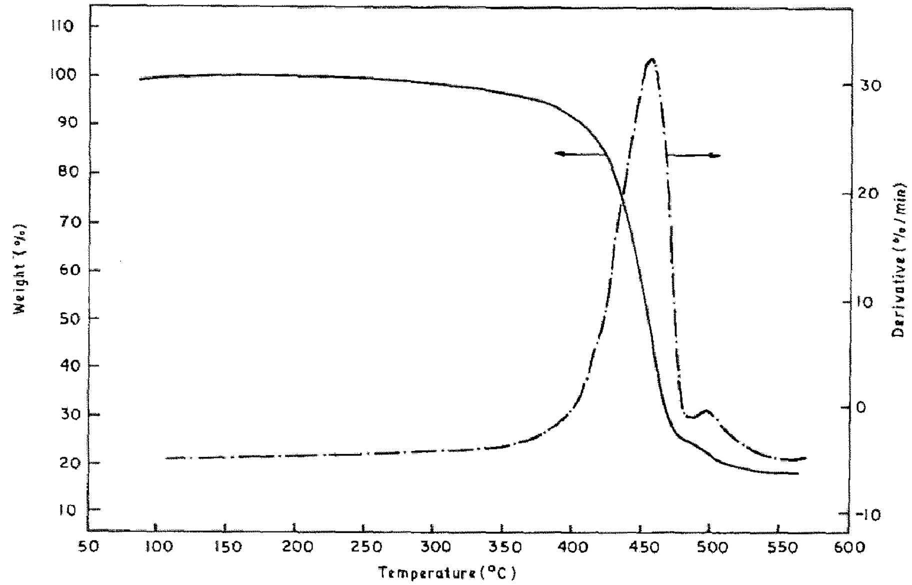

Fig. 4. TGA and DTG curves of 50:50 EMA:PDMS blend.

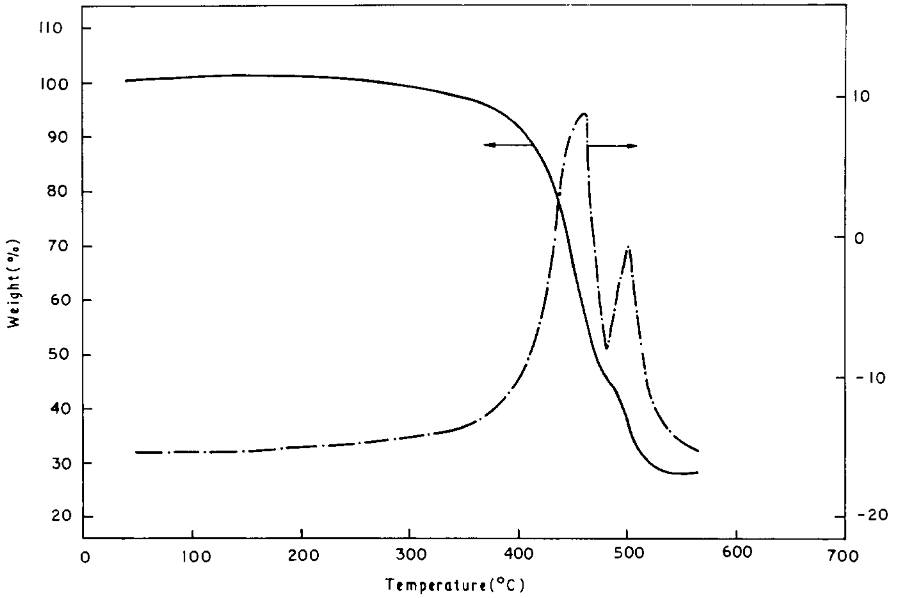

Fig. 5. TGA and DTG curves of 30:70 EMA:PDMS blend.

residue obtained after decomposition reached a miminum (0.78%) in the case of EMA only, and a maximum (≈38%) observed in the case of PDMS. This residue gradually increased with the increase in PDMS rubber content in the blends. The higher residue with PDMS occurs because it is reduced to silica, and also it contained silica as a filler.

Characteristic temperatures determined from the TGA and DTG of the individual components and the blends are summarized in Table 1. The initial decomposition temperature T_i corresponding to 1% decomposition reached a minimum (242°C) with the 70:30 EMA:PDMS blend and a maximum (293°C) with the 30:70 EMA:PDMS blend. This shows that a higher proportion of PDMS in the blends makes them thermally more stable than the individual components.

The DTG curves shown in Figs. 1–5 exhibit maximum rates of weight loss corresponding to the step 1 ($T_{1\max}$) and step 2 ($T_{2\max}$) degradation respectively. In the 50:50 and 30:70 EMA:PDMS blends, the initial weight loss results in a minor peak at 460 and 462°C respectively, while the break-up of the chain results in a major peak around 500 and 504°C respectively.

The final decomposition temperature T_f corresponding to the temperature after which there is negligible further weight loss reaches a maximum for the 30:70 EMA:PDMS blend. This indicates that this blend is less susceptible to thermal degradation during high temperature service conditions. This is once again reflected in T_{50}, i.e. the temperature at which 50% weight loss takes place. This is a maximum for the 30:70 EMA:PDMS

TABLE 1

Parameters evaluated from the thermograms and thermoderivatograms of the blends

Composition of the blends		Intial decomposition temp. T_i (°C)	First maximum decomposition temp. T_{1max} (°C)	Second maximum decomposition temp. T_{2max} (°C)	Final decomposition temp. T_f (°C)	Temp. (T_{50}) at which 50% weight loss takes place (°C)
EMA (wt%)	PDMS (wt%)					
100	0	224	450	–	487	442
70	30	242	457	–	500	454
50	50	266	456	500	550	456
30	70	293	462	504	552	469
0	100	245	464	–	–	547

blend. $T_{2\max}$ and T_f data for 100% PDMS could not be determined with the existing equipment.

A plausible explanation of the higher thermal stability of the 30:70 EMA:PDMS blend is that the labile hydrogen atom at each α-carbon atom adjacent to the ester group of the ethylene–methyl acrylate breaks homolytically to give a H radical and a macroradical A during melt processing under shear. This macroradical, A, is relatively stable and can attack the vinyl group of the PDMS to produce the intermediate radical B or C. The intermediate macroradical B then terminates the initial H radical reaction, forming a new $-CH_2-$ bridge. This is shown schematically in Fig. 6.

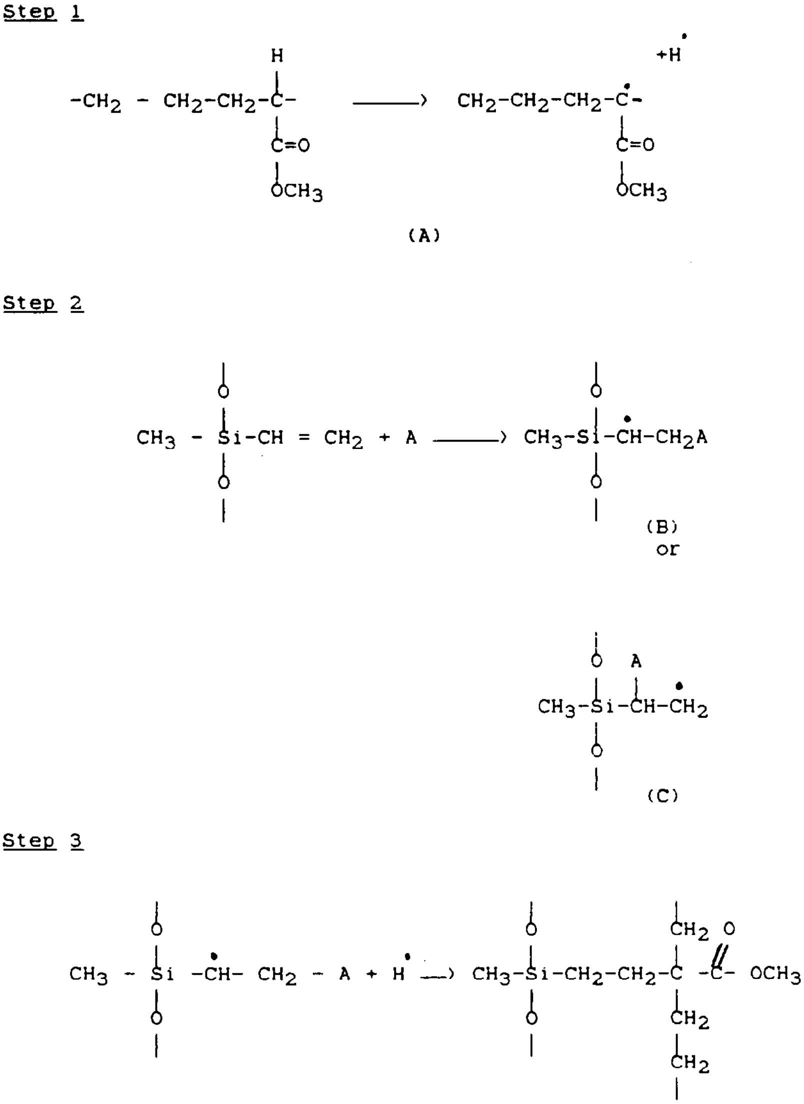

Fig. 6. Reaction scheme for the EMA:PDMS blends.

As a result of the formation of a new carbon–carbon bond between EMA and PDMS, the blend is thermally stable. The 30:70 EMA:PDMS blend is thermally more stable than the other compositions because of the increased number of C–C bonds formed between EMA and PDMS, rather than C–C bonds produced during cross-linking.

The order of the reaction n and the activation energy ΔE for the initial decomposition reactions were determined using the standard kinetic equation

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = A\mathrm{e}^{-\Delta E/RT_w n}$$

where dw denotes the fractional weight change, A is a pre-experimental factor and T and t have their usual meaning [9]. The DTG curves were analysed graphically to determine ΔE and n as described by Freeman and Carroll [10]. The values obtained for the different components and their blends are reported in Table 2.

The activation energies ΔE of the blend components, namely EMA and PDMS, are 45 and 64 kcal mol^{-1} respectively. ΔE values of the blends increase with the incorporation of higher amounts of PDMS in the blends. The experimental values of the activation energies are in good agreement with the values calculated assuming an additivity rule, i.e. the activation energy of thermal degradation of a polymer blend (ΔE_d) is given by the relationship [11]

$$\Delta E_d = w_1\Delta E_1 + w_2\Delta E_2 + \ldots \pm \Delta E$$

where w_1, w_2 etc. are gravimetric fractions of each component in the system. ΔE_1, ΔE_2 etc. are the activation energies of thermal degradation of each component. ΔE is the difference in the energies produced on blending as a result of the formation of polymer–polymer bonds.

In EMA:PDMS blends, the experimental values of ΔE are larger than

TABLE 2

Kinetics parameters evaluated by Freeman–Carroll method

Composition of the blends		Activation energy (kJ mol^{-1})		Order of reaction
EMA (wt%)	PDMS (wt%)	Expt.	Theor.	
100	0	188	188.1	1.0
70	30	222	211.9	1.0
50	50	234	227.8	1.0
30	70	259	243.7	1.0
0	100	268	267.5	1.0

those corresponding to the additivity rule, which is an indication of the presence of strong interactions in the system. The greatest difference between the theoretical and the experimental values is observed for the 30:70 EMA:PDMS blend, which is consistent with the greatest interaction between the blend components in this system. The presence of such strong interactions between the reactive functional groups of EMA and PDMS rubber has been shown earlier to be responsible for the good miscibility of the blend constituents. This finding was also supported by the thermal parameters (Table 1) of 70:30 EMA:PDMS blend. The order of reaction *n* for EMA, PDMS and their blends was found to be near unity in all cases.

CONCLUSIONS

(1) Two stage thermal decomposition was observed in the 50:50 and 30:70 EMA:PDMS blends.

(2) The 30:70 EMA:PDMS blend was found to be the most thermally stable.

(3) Carbon–carbon bonds were formed by the reaction between EMA and PDMS in the blends, and this was most marked in the case of the 30:70 EMA:PDMS blend.

(4) The experimental activation energies are in good agreement with the additivity rule for the blends, but the observed values are higher for the blends.

(5) Activation energy reaches a maximum with the 30:70 EMA:PDMS blend because of strong interactions between the reactive functional groups of EMA and PDMS in the blend, which is evidence of synergism in the blend.

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REFERENCES

1 N. Grassie, I.C. McNeill and I.F. McLaren, Eur. Polym. J., 6 (1970) 679.
2 B. Dodson and I.C. McNeill, J. Polym. Sci., Polym. Chem. Ed., 14 (1976) 353.
3 I.C. McNeill, N. Grassie, J.N.R. Samson, A. Jamieson and T. Straiton, J. Macromol. Sci., Chem., A12 (1978) 503.
4 A. Kaminska and H. Kaczmarek, J. Therm. Anal., 29 (1984) 1017.
5 K.T. Varughese, Kautsch. Gummi, Kunstst. 41 (1986) 1114.
6 M.M. O'Mara, J. Polym. Sci., Part A-1, 8 (1970) 1887.
7 A.K. Bhowmick and H.L. Stephens (Eds.), Handbook of Elastomers — New Developments and Technology, Marcel Dekker, New York, 1988, p. 551.

8 R.N. Santra, S. Roy, A.K. Bhowmick and G.B. Nando, Polym. Eng. Sci., in press.
9 L. Reich and D.W. Levi, in N.M. Bikales (Exec. Ed.), Encyclopedia of Polymer Science and Technology, Vol. 14, Wiley Interscience, New York, 1971, p. 7.
10 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
11 D. Feldman and M. Rusu, Eur. Polym. J., 10 (1974) 41.