JOURNAL OF MATERIALS SCIENCE 18 (1983) 1506–1514

# Effect of silane coupling agents on mechanical and thermal properties of polyester resin concrete

P. MANI, A. K. GUPTA*, S. KRISHNAMOORTHY
*Centre for Materials Science and Technology, Indian Institute of Technology, New Delhi 110016, India*

Polyester resin–quartzite aggregate composites have been investigated for the effect of two silane coupling agents (γ-aminopropyl triethoxy silane and γ-methacryloxy propyl trimethoxy silane) on the mechanical and thermal properties. The integral blend additive method of application of the coupling agent was used in the preparation of the samples. Variation of the thermal stability and the compressive strength with the nature and the content of the silane coupling agent were quite consistent. The properties showed maxima around a certain value of the coupling agent content, which is suggested as the optimum value. Results are also presented on the samples containing an additional filler, namely, the $CaCO_3$.

## 1. Introduction

Composites of inorganic aggregates and polymeric resins, also known as polymer concretes, are finding applications in various civil engineering fields owing to their superior properties when compared with conventional cement-concrete [1–3]. Development of these materials, with desired properties for specific applications, necessitates the knowledge of the various factors that govern or influence their properties.

In addition to the basic factors, namely, the nature of the resin and aggregates and their relative proportion, method of preparation, conditions of curing etc., adhesion between the aggregates and the polymer plays an important role in governing the ultimate properties of the polymer concretes. Adhesion can be improved in various ways, such as (i) by reducing the void volume through the use of an appropriate distribution of aggregate size (i.e. aggregate grading, as it is known in the terminology of civil engineering), (ii) use of small particle fillers (also called microfiller), and (iii) use of silane coupling agents, which improve the bonding at the interface of the aggregates and the polymer matrix.

Polymer concretes using various different kinds of binder (polymeric resins) and the aggregates and other fillers have been developed. The present work is on the polymer concrete prepared with unsaturated polyester resin as the binder and crushed quartzite as the aggregate, which will be called polyester resin concrete (PC). Effects of binder content, aggregate size distribution and curing conditions on the mechanical properties are reported in our previous publications [4, 5]. In this paper, we present a study of the effect of silane coupling agents on the mechanical and thermal properties of the polyester resin concrete. Effect of the microfiller calcium carbonate ($CaCO_3$) on these properties is also presented. The aggregate size distribution (aggregate grading), binder content and curing conditions used for the preparation of the samples of the present investigations were the optimum values found in the previous studies [4, 5].

Two silane coupling agents have been used in varying proportions and the effect of the coupling agent content on the mechanical and thermal properties was studied.

---

*To whom correspondence may be addressed.

0022–2461/83 $03.00 + .12

## 2. Experimental details

### 2.1. Materials

Unsaturated polyester resin, general purpose grade, supplied by Crystic (India) Pvt. Ltd. was used. The catalyst and the accelerator were, respectively, 50% dimethyl phthalate solution of methyl ethyl ketone peroxide and 1% styrene solution of cobalt naphthenate.

The silane coupling agents used had the commercial names Dynasil AMEO and Dynasil MEMO, and were supplied by Nobel Dynamit Co., with the chemical names given below:

(i) Dynasil AMEO ($\gamma$-aminopropyl triethyoxy silane)

(ii) Dynasil MEMO ($\gamma$-methacryloxy propyl trimethoxy silane)

The coarse aggregates used were crushed quartzite with a specific gravity 2.72 and negligible organic impurities and moisture content. The fine aggregate was a siliceous sand (locally known as Badarpur sand) of specific gravity 2.6 and almost nil organic impurities and moisture content. The maximum size of the coarse aggregates used was 10 mm, while that of the fine aggregates was that which passed through British sieve size (BSS) No. 14 sieve and was retained on BSS No. 100 sieve. The aggregate size distribution (grading modulus 6.42 cm$^{-1}$, $D = 4.12$ mm and fineness modulus 4.40) used in these samples is shown in Table I.

TABLE I Aggregate gradings used in the PC samples

| Sieve size | Percentage retained |
|---|---|
| 3/8″ | 0.0 |
| 3/16″ | 45.0 |
| BSS 7 | 18.33 |
| BSS 14 | 3.66 |
| BSS 25 | 7.33 |
| BSS 52 | 16.50 |
| BSS 100 | 9.18 |

### 2.2. Method of preparation

Polyester resin concrete (PC) samples were prepared using 12 wt % of the resin containing the catalyst and the accelerator. The resin and the aggregate were mixed to make a homogeneous mixture. The mixture was then filled into the cylindrical moulds (5 cm diameter and 10 cm height) and compacted. After 24 h curing at room temperature the PC specimens were taken out of the moulds and then further cured at 70° C for 24 h.

The silane coupling agent was applied by the integral blend additive method [6], where the appropriate quantity of the coupling agent was added to the resin mix before the mixing of the

TABLE II Composition and nomenclature of the various samples

| Sample number | Sample nomenclature | Composition (wt %) | | |
|---|---|---|---|---|
| | | Aggregates | Resin mix | $CaCO_3$ |
| 1 | Cured resin | – | 100 | – |
| 2 | Cured resin/0.3* AMEO | – | 100 | – |
| 3 | Cured resin/0.5 AMEO | – | 100 | – |
| 4 | Cured resin/1.0 AMEO | – | 100 | – |
| 5 | Cured resin/1.5 AMEO | – | 100 | – |
| 6 | Cured resin/0.3 MEMO | – | 100 | – |
| 7 | Cured resin/0.5 MEMO | – | 100 | – |
| 8 | Cured resin/1.0 MEMO | – | 100 | – |
| 9 | Cured resin/1.5 MEMO | – | 100 | – |
| 10 | PC | 88 | 12 | – |
| 11 | PC/0.3 AMEO | 88 | 12 | – |
| 12 | PC/0.5 AMEO | 88 | 12 | – |
| 13 | PC/1.0 AMEO | 88 | 12 | – |
| 14 | PC/1.5 AMEO | 88 | 12 | – |
| 15 | PC/0.3 MEMO | 88 | 12 | – |
| 16 | PC/0.5 MEMO | 88 | 12 | – |
| 17 | PC/1.0 MEMO | 88 | 12 | – |
| 18 | PC/1.5 MEMO | 88 | 12 | – |
| 19 | PC/$CaCO_3$ | 82 | 12 | 6 |
| 20 | PC/$CaCO_3$/1.0 AMEO | 82 | 12 | 6 |
| 21 | PC/$CaCO_3$/1.0 MEMO | 82 | 12 | 6 |

*Number indicates the amount of silane coupling agent (by wt % of resin) added as integral blend additive.

TABLE III Compressive strengths ($\sigma_c$) of the various PC samples

| Sample number | Sample | $\sigma_c$(kg cm$^{-2}$) | Coefficient of variaton (%) |
|---|---|---|---|
| 10 | PC | 420 | 3.8 |
| 11 | PC/0.3* AMEO | 431 | 5.0 |
| 12 | PC/0.5 AMEO | 447 | 5.2 |
| 13 | PC/1.0 AMEO | 476 | 5.4 |
| 14 | PC/1.5 AMEO | 464 | 4.0 |
| 15 | PC/0.3 MEMO | 465 | 4.6 |
| 16 | PC/0.5 MEMO | 530 | 5.9 |
| 17 | PC/1.0 MEMO | 540 | 5.0 |
| 18 | PC/1.5 MEMO | 493 | 3.2 |
| 19 | PC/$CaCO_3$ | 510 | 3.5 |
| 20 | PC/$CaCO_3$/1.0 AMEO | 554 | 3.9 |
| 21 | PC/$CaCO_3$/1.0 MEMO | 693 | 5.9 |

*Number indicates the amount of silane coupling agent (by wt % of resin) added as integral blend additive.

aggregates to the resin. The proportion of the silane coupling agent was varied from 0.3 to 1.5 wt % of the resin.

The microfiller $CaCO_3$, wherever used, was added in the stipulated proportions to the aggregate before mixing the aggregates and the resin.

The composition and the nomenclature of the various samples used in this study are described in Table II.

## 2.3. Measurements

The compressive strength was measured on an

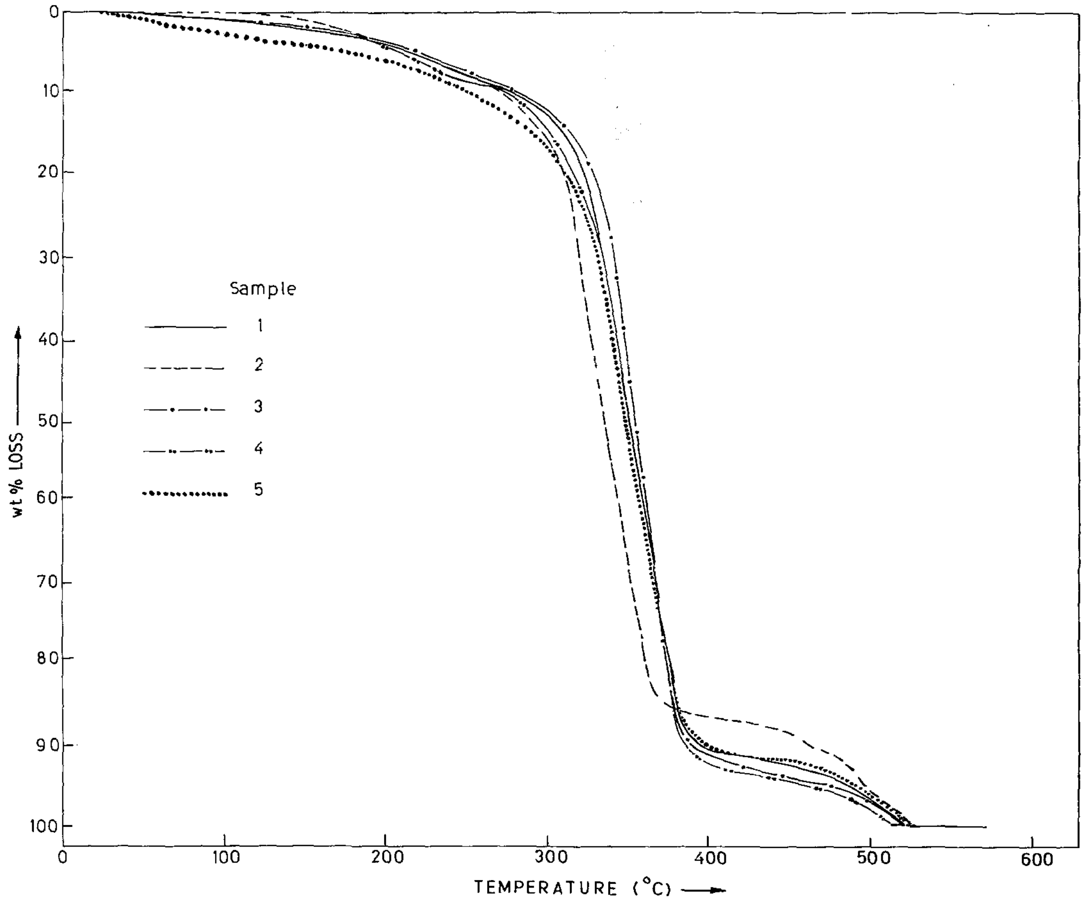

*Figure 1* TGA thermograms of the various cured polyester resin samples without any coupling agent and with silane coupling agent AMEO.

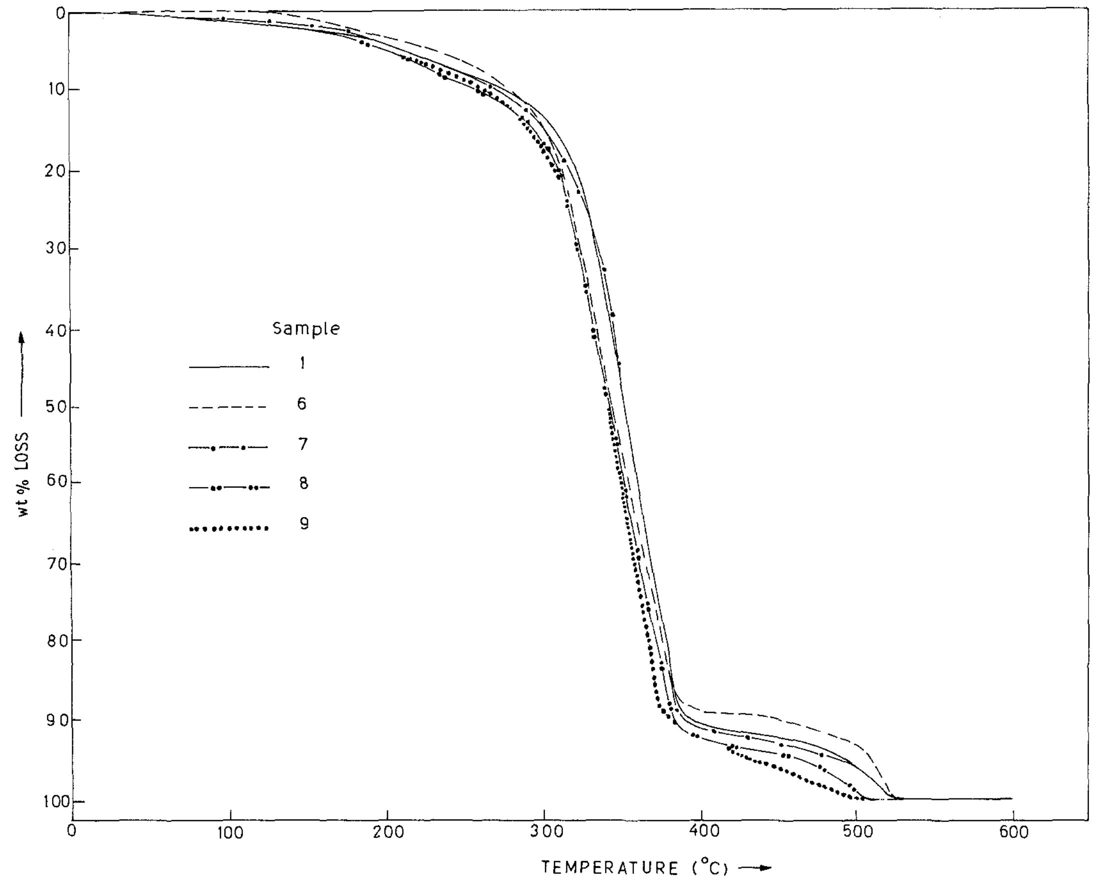

*Figure 2* TGA thermograms of the various cured polyester resin samples without any silane coupling agent and with silane coupling agent MEMO.

Avery Compression Tester, according to BS 1881: Part 4: 1970 using the loading rate 120 kg cm$^{-2}$ min$^{-1}$. Measurements were done on three to five samples in each case. Consistency of the results was quite good, as was apparent from the coefficient of variation (which was 3 to 6% in all the cases) indicated in these results and shown in the subsequent section.

Thermogravimetric measurements were done on a Dupont Thermal Analyzer 990-TGA-951 at a programmed heating rate, 10° C min$^{-1}$, in a static air atmosphere. The thermobalance and the thermocouple were precalibrated with standard materials. Thermograms were recorded in the temperature range of room temperature to 600° C. Reproducibility of the results was ascertained by recording at least three runs in each case, using a constant sample weight (15 mg) in all cases. Some effect of moisture content on the reproducibility was noted, which was overcome by proper drying in a vacuum oven and subsequent storage in a dessicator.

Thermal stability, in terms of the integral procedural decomposition temperature (IPDT), was calculated according to the method suggested by Doyle [7]. Initial decomposition temperature (IDT) was not so precisely located on these thermograms, hence the temperature at 10 wt % loss, $T$ (10% loss), has been used as a parameter analogous to IDT. Activation energy of degradation ($E$) was calculated from the thermograms according to the standard procedure [8].

## 3. Results and discussion

### 3.1. Mechanical properties

Compressive strength ($\sigma_c$) of these various PC samples are shown in Table III. It is apparent on these results that the use of the silane coupling agent increases $\sigma_c$. The increase in $\sigma_c$ is higher in the case of the coupling agent MEMO. Evidence for better bonding at the aggregate surface in case of MEMO than AMEO is provided by infrared spectroscopic study on these PC samples [9]. A further noteworthy point of these results is that

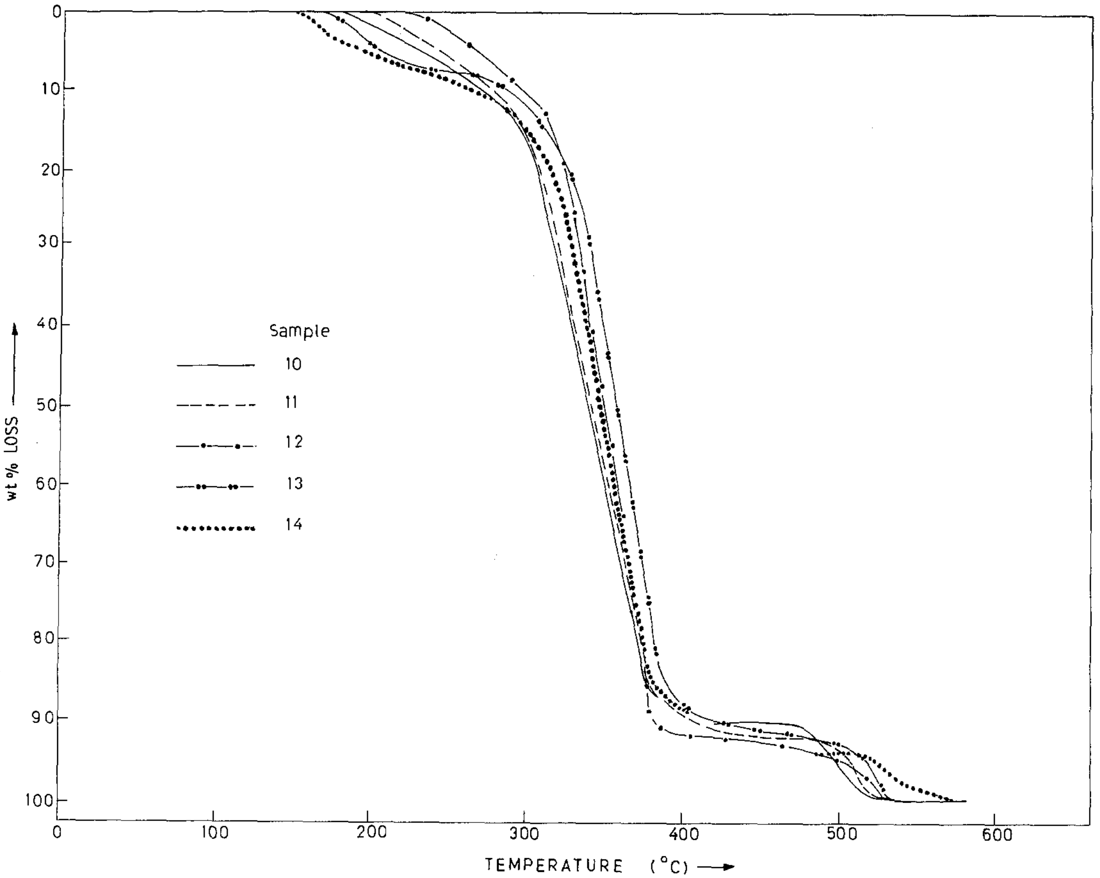

*Figure 3* TGA thermograms of the various PC samples without any coupling agent and with the silane coupling agent AMEO.

with increasing coupling agent content, $\sigma_c$ first increases, passes through a maximum and then decreases beyond a 1.0% level of the coupling agent content for both AMEO and MEMO. This suggests that the optimum amount of coupling agent is around 0.5 to 1.0 wt% of the resin when applied as an integral blend additive. In the other methods of application of the coupling agent, namely, the pretreatment of aggregates through aqueous or methanol solution, the optimum amount of coupling agent used might be different from this value. Owing to the convenience involved, the integral blend additive method is preferable.

Use of the microfiller, $CaCO_3$, produces a considerable increase in $\sigma_c$ even when no silane coupling agent is used (compare samples 10 and 19 in Table III). Owing to its small particle size, $CaCO_3$ fills the voids between the aggregates and thus produces a more compact structure with better adhesion between the aggregates. Use of the silane coupling agents further improves the compressive strength of PC samples containing $CaCO_3$. Here again $\sigma_c$ is higher for the case of coupling agent MEMO than AMEO (compare samples 20 and 21 in Table III).

## 3.2. Thermal properties

TGA thermograms for the various samples are shown in Figs. 1 to 4. The lowest plateau above 500° C represents 100 wt% loss of the polyester component. Values of $T$ (10% loss), IPDT and $E$ are shown in Table IV, and their variations with coupling agent content are shown in Fig. 5.

In the case of cured resin without aggregates (i.e. samples 1 to 9), a decrease in thermal stability with increasing coupling agent content is apparent from the values of $T$ (10% loss), IPDT and $E$. Such behaviour is observed for both the coupling agents AMEO and MEMO.

The lower thermal stability of the cured polyester resin in the presence of the silane coupling agents indicates that the coupling agent hampers the cross-linking and thus reduces the thermal

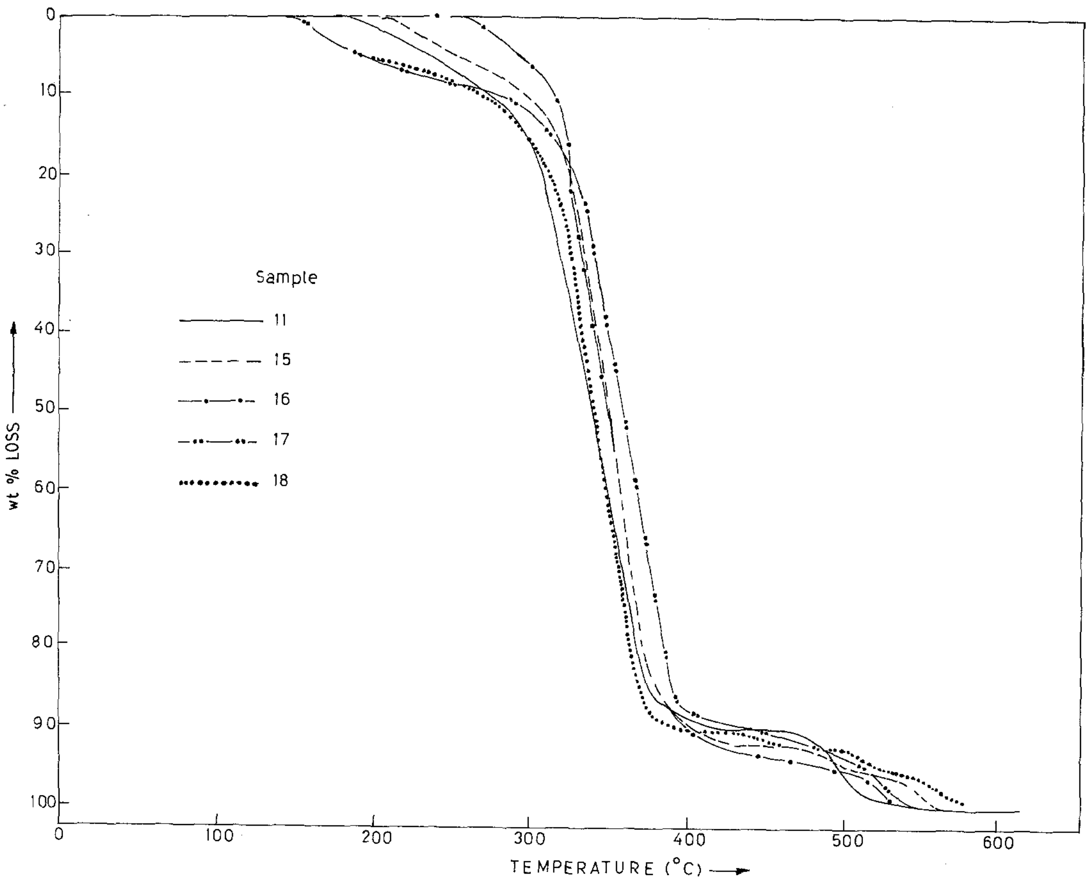

*Figure 4* TGA thermograms of the various PC samples without any coupling agent and with the silane coupling agent MEMO.

stability of the cured resin. Owing to the presence of the coupling agent molecules, the cross-linking of the polyester may not be possible at some of the cross-linking sites. Moreover, such an effect should increase with increasing proportion of silane coupling agent, as evidenced by these results.

PC sample without the coupling agent (sample 10) shows $T$(10% loss) and $E$ values to be the same as those of the cured resin without coupling agent (sample 1); the IPDT, however, is slightly different for the two samples. This suggests that the thermal stability of the cured polyester in the PC sample (i.e. in the presence of the aggregates) is not much different from that of the cured polyester resin without the aggregates. If we consider the structure of PC to consist of two phases, namely, the aggregate and the polyester domains, then the PC without the silane coupling agent would differ from the PC with the silane coupling agent in their structure at the interface. The surface properties of the polyester domains in these two cases would be different owing to the occurrence of chemical bonding with the aggregate surface, in the case of PC with the silane coupling agent. Thermal stability of polyester domains would be a combined effect of the surface energy and the properties of the bulk, hence, the observed higher thermal stability of PC with the silane coupling agent than PC without the silane coupling agent may provide indirect evidence for the interfacial chemical bonding in the case of PC with the silane coupling agent.

Thermal stability of the PC with the silane coupling agents (samples 11 to 18) was in general higher than that of the PC without the coupling agent (sample 10). $T$(10% loss), IPDT and $E$ showed variation with coupling agent content as represented in Fig. 5. Maxima in $T$(10% loss) and $E$ are observed around 0.5% coupling agent content. IPDT, however, showed somewhat broader maxima in the range 0.5 to 1.0% coupling agent content. At higher coupling agent content (> 1.0%), IPDT, $T$(10% loss) and $E$ decreased again.

TABLE IV TGA data for the cured resin and the PC samples

| Sample number | Sample | $T$ (10% loss) (° C) | IPDT (° C) | $E$ (kcal mol$^{-1}$) |
|---|---|---|---|---|
| 1 | Cured resin | 280 | 359 | 42 |
| 2 | Cured resin/0.3* AMEO | 275 | 350 | 43 |
| 3 | Cured resin/0.5 AMEO | 270 | 348 | 40 |
| 4 | Cured resin/1.0 AMEO | 260 | 344 | 37 |
| 5 | Cured resin/1.5 AMEO | 255 | 342 | 32 |
| 6 | Cured resin/0.3 MEMO | 277 | 353 | 40 |
| 7 | Cured resin/0.5 MEMO | 272 | 346 | 37 |
| 8 | Cured resin/1.0 MEMO | 260 | 343 | 35 |
| 9 | Cured resin/1.5 MEMO | 255 | 341 | 30 |
| 10 | PC | 280 | 348 | 42 |
| 11 | PC/0.3 AMEO | 285 | 345 | 45 |
| 12 | PC/0.5 AMEO | 300 | 358 | 50 |
| 13 | PC/1.0 AMEO | 288 | 362 | 42 |
| 14 | PC/1.5 AMEO | 255 | 351 | 37 |
| 15 | PC/0.3 MEMO | 300 | 359 | 45 |
| 16 | PC/0.5 MEMO | 320 | 362 | 48 |
| 17 | PC/1.0 MEMO | 285 | 366 | 40 |
| 18 | PC/1.5 MEMO | 265 | 351 | 34 |
| 19 | PC/$CaCO_3$ | 270 | 337 | 45 |
| 20 | PC/$CaCO_3$/1.0 AMEO | 260 | 347 | 46 |
| 21 | PC/$CaCO_3$/1.0 MEMO | 260 | 336 | 47 |

*Number indicates the amount of silane coupling agent (by wt % of resin) added as integral blend additive.

Fig. 5. reveals an interesting point about the correspondence between the three TGA parameters: IPDT, $T$ (10% loss) and $E$. The similarity of the curves for $E$ and $T$ (10% loss) is remarkable, while they differ from IPDT in peak-width. IPDT shows broad maxima between 0.5 and 1.0% coupling agent content, whereas $E$ and $T$ (10% loss) show less broad maxima at 0.5% coupling agent content. However, the curves representing compressive strength have a greater resemblance with those of IPDT, than $E$ or $T$ (10% loss). This implies that out of the three parameters representing the thermal stability measured from thermogravimetric analysis, IPDT has a better correlation with the mechanical properties (compressive strength of the PC samples).

Since, in these samples the silane coupling agents were added as integral blend additives, it might be that only a certain portion of it could migrate to the aggregate surface. Hence an excess amount of the silane would be normally required for achieving the maximum bonding between the aggregates and the resin matrix. At lower values of the coupling agent content (i.e. $< 0.5\%$), bonding at the interface (chemical bonding through the silane coupling agent) might be insufficient, which seems supported by the observation of poorer mechanical properties of the composites with such low coupling agent contents (see Fig. 5 and Table III). At coupling agent contents higher than the optimum (i.e. $> 1.0\%$), there is a possibility that a partial amount of the silane added may undergo self condensation after hydrolysis and thus leading to the deposition of thick layers of oligomeric silanols which form distinct interface regions between the aggregates and the resin matrix. Thus the properties of the interface may govern the mechanical properties of the PC [10].

Thermal stability of PC with $CaCO_3$ (sample 19) is somewhat lower than that of PC (sample 10). Use of the silane coupling agents in the PC with $CaCO_3$ produced an insignificant change in the thermal stability whereas the compressive strength was sufficiently improved (Tables III and IV). The $CaCO_3$ particles, which give more compact structure by reducing void volume, may be bound only through physical bonds. The reactive ends of the silane coupling agent, which would fall in contact with the surface of $CaCO_3$ particles, may not form chemical bonds with the $CaCO_3$ surface and would not be able to reach the aggregate surface. Hence in the structure of the PC samples with $CaCO_3$ the chemical bonding at the aggregate surface due to the silane coupling agent might be of a lower degree but the physical bonding in the structure is stronger. This might be the cause of the observed better mechanical properties and lower improve-

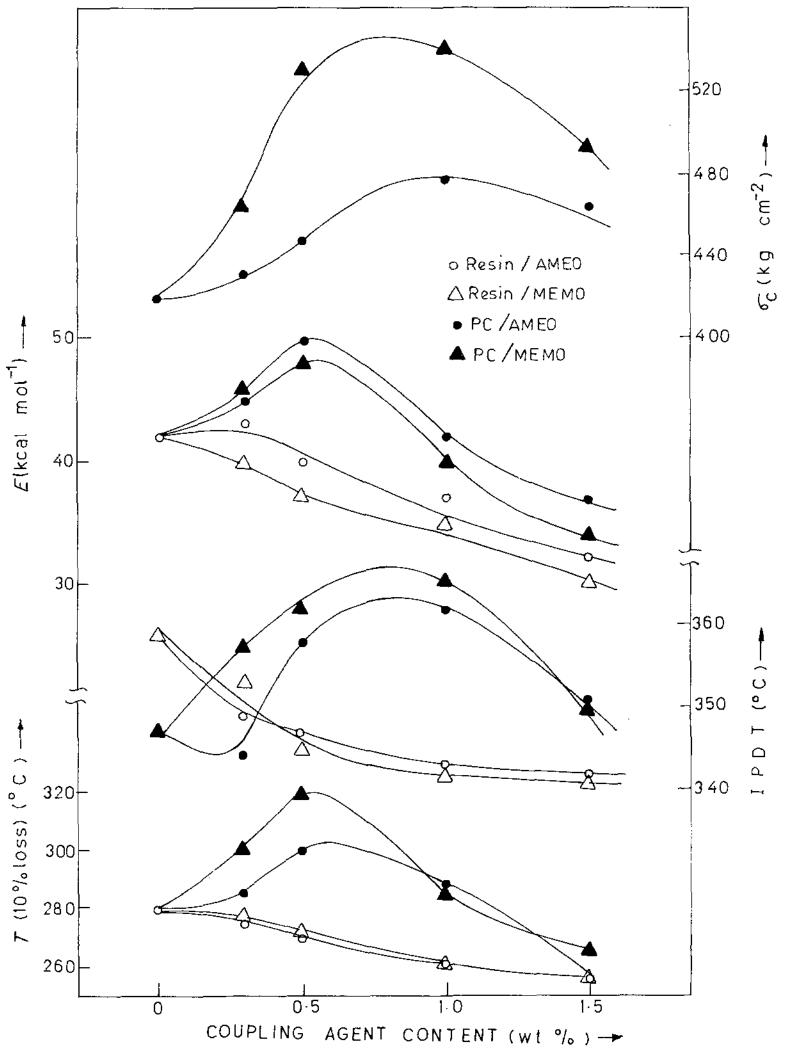

*Figure 5* Variation of IPDT, $T$ (10% loss), $E$ and the compressive strength with coupling agent content for cured polyester resin and the PC samples.

ment in thermal stability of the PC samples containing $CaCO_3$ filler.

## 4. Conclusions

These results show that out of the two silane coupling agents used, the coupling agent MEMO produced better mechanical properties of the composite than the coupling agent AMEO. Compressive strength of the polyester resin concrete varied with coupling agent content. Maxima were obtained around 0.5 to 1.0% coupling agent content for both the coupling agents.

Use of microfiller $CaCO_3$ increased the compressive strength of polyester resin concrete even when no silane coupling agent was used; the improvement was further enhanced by the inclusion of the silane coupling agents.

Thermal stability of the polyester resin concrete was increased on the application of the silane coupling agents, and its variation with coupling agent content showed maxima at around 0.5 to 1.0%.

## References

1. J. T. DIKEOU, "Polymers in Concrete" (The Concrete Society Publication, Lancaster, 1976) p. 1.
2. R. K. GHOSH, Y. R. PHULL and C. S. PANT, SP-58, "Polymers in Concrete" (ACI Publication, Michigan, 1978) p. 103.
3. Y. OHAMA, in preprint of Third International Congress on Polymers in Concrete, Koriyama, Japan (1981) p. 634.
4. P. MANI, S. KRISHNAMOORTHY and A. K. GUPTA, in Proceedings of the National Seminar on Polymeric Materials and their Engineering Application, Trivandrum, December 1981, Section I, Paper 2, pp. 15–23.
5. P. MANI, S. KRISHNAMOORTHY and A. K. GUPTA, in Proceedings of the National Symposium on Binder Economy and Alternate Binders in Road and Building Construction, New Delhi, November

1981, (Central Road Research Institute, New Delhi) Section III, pp. 1–13.

6. S. STERMAN and J. G. MARSDEN, SPI 18th Annual Technical Conference, Chicago, February 1963 (The Society of Plastics Industry Inc., New York) Section 1D, pp. 1–18.
7. C. D. DOYLE, *Anal. Chem.* 33 (1961) 71.
8. S. R. DARWADKAR and M. D. KARKHANWALA, *J. Thermal Anal.* 2 (1969) 1049.
9. P. MANI, A. K. GUPTA and S. KRISHNAMOORTHY, *J. Mater. Sci. Lett.* 1 (1982) 467.
10. R. V. SUBRAMANIAN and KUANG-HUA H. SHU, SPI 34th Annual Technical Conference, Washington DC, February 1979 (The Society of Plastics Industry Inc., New York, 1979) Section 17-C pp. 1–10.

*Received 1 September*
*and accepted 12 November 1982*