S U M M A R Y

The thesis comprises of four chapters i.e. introduction and literature survey, experimental, results and discussion, and conclusions and future scope. Four types of composites including electrically conducting composites, heat ablating composites, bone grafting synthetic HAp-composites and dental composites have been developed and investigated in present work. The first two composites have been categorised as advanced composites and last two as bio-composites. The following is the gist of the development and investigation on advanced and bio-composites studied under the present work.

(a) Electrically Conducting Composites : Aluminium coated short fibre glass with various volume fractions i.e. 1%, 5%, 10%, 15%, 20%, 30% and 40%, have been incorporated in 20% weight EPDM toughened polypropylene by melt mixing process in a Brabender Plasti-Corder and the short fibre glass reinforced polypropylene composites have been developed by melt blending at 184°C. Cylindrical and flat specimens have been fabricated by hot pressing at 170°C in a die-punch type mould and the d.c. electrical conductivity, E.M.I. - shielding efficiency, density, porosity, hardness, toughness, and acousto-ultrasonic study of the composites have been performed. The d.c. conductivity results reveal that a

critical volume fraction of 5% of fibre loading induces electrical conductivity in polypropylene thermoplastics. Higher aspect ratio fibres have been found to exhibit conductivity in the composite even at lower volume fraction of staple fibre loading in the matrix. But the mechanical properties of these composites were observed to be dependable on bond quality of polypropylene matrix, critical fibre length, orientation of fibre and the ductility of the polymer matrix. Since, aluminium has got poor wettability with polypropylene matrix hence surface treatments were given to aluminium coated staple fibres for improving wetting properties and E.P.D.M. was added to the matrix to induce ductility in the composites. From SEM study it is obvious that cracks propagate along the fibre in case of weak interface; but in case of strong bonding cracks proceed across the matrix. The E.M.I. shielding of 26dB has been found in composites having 5 volume percent of aluminium coated short glass fibre. A correlation has been established between stress-wave factor and the resistivity of the composites. The density, porosity, micro-hardness and moisture absorption of the composites have also been correlated with weight percentage of the filler in the composites. The variation of resistivity of the composites with temperature has been observed as part of this research.

(b) **Heat Ablating Composites** : Ablative materials have been developed by processing high silica phenolic composites in different curing conditions. Since, 'phenol-formaldehyde' resin contains high volatile matter which offer resistance in casting and temperature-curing by usual process, hence high silica phenolic products were made by using high silica cloth as reinforcing agent and phenol-formaldehyde as resin matrix and cured at various temperature cycles in an autoclave with controlled pressure and vacuum in order to optimise the effect of degree of polymerisation on various properties of silica phenolic composites, like, thermal conductivity, burn through time, specific heat, density, hardness, tensile strength, flexural strength, etc. for critical evaluation. The comparison Table I has highlighted that the sample no. N was having highest 'burn through time', 'flexural strength', 'tensile strength' and 'hardness' as compared to sample nos. H, F and P. But such change could not be noticed in the values of density and specific heat for the above samples, whereas the thermal conductivity and the void content were significantly low for sample no. N compared to any other samples tested. Also, the SEM-microphotograph showed a good bonding between the Refrasil cloth fibre and the resin matrix for sample no. N due to the formation of proper interface between the fibre and phenol-formaldehyde resin.

On the other hand, weak interface could be observed for sample no. P which may be due to degradation of resin matrix while curing at 180°C. Since, the time of curing was less so total degradation could not occur and hence, the performances did not come down significantly except the burn through time.

(c) Bone Grafting Synthetic HAp-Composites : The synthesis of $[Ca_{10}(PO_4)_6(OH)_2]$ was performed by the addition of AR-grade of an aqueous solution of $(NH_4)_2HPO_4$ in reagent grade NH_4OH (pH=12) to an aqueous solution of AR-grade of $Ca(NO_3)_2$ in reagent grade of NH_4OH (pH=12) at the temperature of 80°C. Synthetic hydroxyapatitel, the amorphous precipitate, was washed with the ions of alumina, magnesia,zirconia and vanadium separately under pH fluctuating conditions for 10-minutes followed by filtering and drying prior to heat-treatment. All the above samples were heat-treated at various temperatures upto 800°C to transform amorphous phases to crystalline phases, for achieving better mechanical properties. It has been shown by Heughebaert that the composition of the crystalline phase after the completion of its formation from the amorphous calcium phosphate precipitate was actually $[Ca_9(HPO_4)_x(PO_4)_{6-x}(OH)_x]$. Hence, this defective apatite structure can be avoided by directly precipitating from a boiling solution, and not at room temperature. This

experiment was performed at 80°C instead of boiling condition in order to avoid formation of hydrated monetite by reaction of synthesized pure HAp with very low Mg^{+} ions leaching out from the glass container used for the reaction. The resultant phase may have contributed to the error in the lattice parameter measurement for pure HAp. The carbonate ions content was determined by analysing the infrared absorption bands of phosphate and carbonate at 962 cm^{-1} and 870 cm^{-1} respectively. Magnesium ions, in the bone inorganic phase and in the body fluids, can play an important role in the process of recrystallization.

Table II shows, that the incorporation of magnesia or vanadium has little effect in enhancing the strength of synthetic bone graft substitute materials as compared to pure alumina or pure zirconia doped artificial bone graft substitutes. In-vitro studies have also been done on bone graft substitute at various pH conditions.

(d) Dental Composites : Biological apatite has been replacedby synthetic hydroxyapatite (HAp). HAp has been synthesized by wet-chemical reaction of pure grades of an aqueous solution of ammonium phosphate and pure calcium nitrate in reagent grades of ammonium hydroxide at the temperature of 80°C. Then the synthetic HAp was filtered and dried and coated on alumina ceramic dental implants followed

by in-vitro heat-treatment of the HAp-coated ceramic implants.

Table III shows the heat treatment effects of the synthetic HAp-coated ceramics. Crystallization of HAp-coating starts from 860°C upto 1200°C, forming beta-tricalcium phosphate (β - TCP). Further increase in temperature beyond 1200°C results in, formation of both, β and α - TCP. But heat-treatment was found to have no effect on the structure of the core material i.e., alpha alumina. Table IV highlights the lattice parameters of HAp and beta-tricalcium phosphate prepared by heat-treatment of synthetic hydroxyapatite. The properties of the coated synthetic hydroxyapatite after in-vitro heat-treatment have been tabulated in Table V.

In order to eliminate the structural defects, the HAp has been synthesized at 80°C which enhances the performance. In-vitro heat-treatment effects HAp coated alumina have ensured proper crystallization as well as stress-free dental implants. The various structures have been examined by XRD and SEM.

Table -I. Comparison of various test results of heat ablating composites.

Sl. No.	Sample No.	Density (gm/cc)	Porosity (%)	Hardness (BARCOL)	Tensile Strength (MPa)	Flexural Strength (MPa)	Burn Through Test (Sec.)	Thermal Conductivity (Cal/cm/sec/°C)	Specific Heat at 100°C (Cal/gm/°C)
1	H	1.47	3.2	32	-	-	52.18	6.70×10^{-4}	0.33
2	F	1.52	5.6	61	91.03	149.79	53.80	7.00×10^{-4}	0.30
3	P	1.49	1.7	65	106.14	169.42	67.74	6.98×10^{-4}	0.34
4	N	1.48	1.2	69	108.79	176.28	104.76	5.66×10^{-4}	0.34

Where, H = Half cured specimen,
F = Full cured specimen,
P = Post cured specimen,
N = New cycle cured specimen.

Table - II. Physical and mechanical properties of artificial bones.

Properties	Synthetic apatite	Alumina doped synthetic apatite	Zirconia doped synthetic apatite	Magnesia doped synthetic apatite	Vanadium doped synthetic apatite
Bulk density (gm/cc)	2.04	2.58	2.72	2.37	2.88
Open porosity (%)	13.97	19.30	21.20	16.78	15.45
Hardness (Shore scale-A)	87.50	92.00	90.00	86.50	89.00
Shrinkage (%)	1.53	2.12	2.43	1.82	1.65
Glass transition temperature (°C)	547.00±2	562.00±2	560.00±2	550.00±2	552.00±2
Crystallization temperature (°C)	665.00±2	710.00±2	710.00±2	698.00±2	695.00±2
Flexural strength (MPa)	158.30±7	186.60±7	210.00±7	173.80±7	166.00±7
Elastic modulus (GPa)	16.80±2	17.60±2	17.80±2	17.00±2	16.90±2
Compressive strength (MPa)	186.70±10	212.50±10	223.80±10	200.30±10	197.80±10
KI_C (MPa.$m^{\frac{1}{2}}$)	3.40	3.82	3.94	3.61	3.76

N.B. : All the above experimental results are average values of 5 samples with 95% confidence limit.

Table - III. Crystalline phases obtained by in-vitro heat-treatment of hydroxyapatite coated alumina dental implants.

Heat Treatment temperature (°C)	Obtained Phases of coated material of dental implants	Obtained Phases of core material of dental implants
100	HAp	Alpha alumina
500	HAp	Alpha alumina
600	HAp	Alpha alumina
700	HAp	Alpha alumina
800	HAp	Alpha alumina
900	HAp >> β-TCP	Alpha alumina
1000	HAp >> β-TCP	Alpha alumina
1100	HAp >> β-TCP	Alpha alumina
1200	HAp >> β-TCP	Alpha alumina
1300	HAp >α-TCP > β-TCP	Alpha alumina

N.B. >> = much more than

> = more than

Table - IV. Lattice parameters of the coated HAp and beta-tricalcium phosphate obtained by heat-treatment of the synthetic hydroxyapatite.

Phase	Lattice constants	
	a(Å)	c(Å)
HAp	9.410	6.888
Beta-TCP	10.430	37.350

Table - V. Properties of the synthetic hydroxyapatite used for coating on dental implants.

Properties	Values obtained
Bulk density (gm/cc)	2.34
Hardness (Shore A)	91.00
Shrinkage (%)	1.8
Compressive strength (MPa)	192.50
KI_c ($MPa.m^{\frac{1}{2}}$)	3.68