The changing frontiers in thermoplastics and elastomer technology

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ABSTRACT

Confronted with the demands of improved efficiency and economy of operation, safer environment, energy conservation and increasing needs of mankind for newer materials, commercial polymers are undergoing a constant shift in their technological base. The most visible advances are the following disciplines of polymer science: (a) new generation of catalysts to produce established polymers; (b) property modification of polymers using post polymerization techniques; (c) multicomponent polymer systems such as coplymers, polyblends and composites; (d) new polymer devolpment for speciality applications; (e) new polymer conversion techniques; and (f) development of engineering capabilities for the design and computer assisted operation of large polymerization reactors.

The present paper attempts with illustrate this change in technological base with a few chosen examples, such as (a) new process technologies based on improved catalysts for LDPE, PP and high -cis-polybutadiene; (b) new developments in ultra-high modulus polymers based on crystalline thermoplastics such as PP and HDPE via post polymerization techniques; and (c) developments in surface energy modifications of inorganic filler with a view to enhance its compatibility with organic polymers in a composite matrix.

INTRODUCTION

THE technology of synthetic polymers has entered a distinct phase since the early seventies, namely that of the resource and husbandry period. The objectives now are to improve, cheapen and assure supplies of needed products by improved efficiency and economy of operation, energy conservation, better design and substitution of scarce raw materials with more abundant feedstocks. Additionally, the technology has to contend with the more stringent standards of cleaner environment and safer occupational health, which society now imposes on industry.

Confronted with these challenges, commercial polymers are undergoing a constant shift in their technological base. The most visible advances are in the following disciplines of polymer science: (a) newer catalysts to produce established polymers (b) pro perty modification of polymer using post polymerization techniques (c) multicomponent polymer systems such as copolymers, polyblends and composites (d) newer polymers for speciality applications (e) newer techniques of polymer processing and (f) development of engineering capabilities for the design and computer assisted operation of large polymerization reactors.

The rapidly moving frontiers in thermoplastic and elastomer technology are illustrated in chart I with reference to the commercially important large volume polymers. This paper presents a brief survey of some of these developments with specific examples drawn from recent literature.

NEW PROCESS TECHNOLOGIES

A. Low density Polyethylene : LDPE has become the most widely used general purpose plastic in the world. From film to pipe to wire and cable coatings, the plastic has found myriad end uses. Over the years, the conventional high pressure LDPE technology (column 1, Table I) has undergone some changes. These include a 12 fold increase in name-plate capacities, better reactor configurations and an increase in per-pass conversion from 15-18% to 30-35% by increased operating pressures. High conversion LDPE processes based on autoclave reactors have increased conversions to 22% per pass even at relatively lower pressures and temperatures (1100-1400 kg/cm^2, 150-200°C)[1].

However, the recent announcement of a low pressure LDPE process has dramatically altered the technological scene[2]. Based on the patents granted to Union Carbide, it is surmised that these LDPE resins are actually ethylene-butene-1 copolymers prepared in a fluidised bed using a silica supported catalyst comprising of chromium oxide, titanium isopropoxide and ammonium hexafluorosilicate (Column 2, Table I)[3].

CHART I
INDUSTRIAL POLYMERS AND KEY TECHNOLOGY CHANGES

1.	Low Density Polyethylene	New process technology
2.	PVC	Large Reactors (200 m^3); Automated computer controlled production
3.	High Density Polyethylene	New process technology Property modification by post-polymerization techniques High force processing of UHMW-PE by Ram Extrusion, Compression Moulding and Forging
4.	Polystyrene	Multicomponent Styrenic polymers such as block copolymers and polyblends
5.	Polypropylene	New process technologies Filled composites based on PP Newer more important additives for PP stabilization Newer processing techniques Solid phase pressure forming (Shell) for thermoforming thin walled packing containers Oriented PP blow Moulding (Phillips ORBET process) for OPP containers Stamping, OPP films and foam moulding
6.	Polyesters	Injection mouldable and glass fibre reinforced thermoplastic polyesters such as RYNITE poly (ethylene terephthalate) (DuPont) and poly (tetramethylene terephthalate). 45% glass fiber reinforced RYNITE is one of the stiffest plastics ever developed (Flex. mod : 1.4 x 10^{10} Nm^{-2})
7.	Elastomers	Larger capacity plants; computer controlled operation. New Stereospecific Polymerization catalysts. Improved elastomeric compositions based on new catalysts such as alternating (ACN-co-butadiene), alternating (Protylene-co butadiene) Thermoplastic-elastomers based on block copolymers of butadiene or isoprene with styrene

The low pressure process offers a 50% reduced capital costs, 75% reduction in energy costs as a result of savings in compressor pump h.p. and elimination of extrusion and pelletizing steps, space savings, reduced noise pollution and safer operations.

In a sense, the low pressure process complements the high pressure LDPE (d = 0.91 — 0.93 g/cc) and HDPE (d = 0.94 — 0.96 g/cc) and identifies a third type of polyethylene, now termed ''Linear lows (d = 0.92 — 0.94 g/cc). This density range is inaccessible in the conventional LDPE and HDPE processes. Additionally, the product is obtained as granules from the reactor and is capable of being processed in the same form.

The idea of using a comonomer to reduce densities is not new and has been practised for a number of years in HDPE production. However, it was found difficult to lower resin density much below 0.925 using conventional processes without creating undesirable effects on other product properties.

The resin from the new process is claimed to be suitable for a variety of LDPE applications such as injection moulding, blown films, wire and cable products, blow moulding, pipes and rotational moulding.

B. High Density Polyethylene : The low pressure LDPE processes is a logical outgrowth of the gas phase HDPE technology, which has already attained commercial success[4] (column 3, Table I). The catalyst comprises of a chromate ester of bis(triphenyl) silanol and organoaluminium alkoxide supported on high surface area silica. Under appropriate conditions the process is capable of producing ultra high molecular weight polyethylene (MFI 0.01 — 01).

TABLE I — CHANGING FRONTIERS IN POLYETHYLENE TECHNOLOGY

	High Pressure-LDPE (ICI)	**Low Pressure-LDPE (Union Carbide)**	**Low Pressure-HDPE (Union Carbide)**
1. Feed	Ethylene	Ethylene + Butene-1 (93:7)	Ethylene + Butene-1
2. Conditions	350°C/3500 kg cm^{-2}	95°C/7-21 kg cm^{-2}	88°C/7 kg cm^{-2}
3. Mode	Bulk Polymerization in a tubular plug flow reactor	Bulk Polymerization in a fluidized bed reactor	Bulk Polymerization in a fluidized bed reactor
4. Catalysts	O_2 or peroxides	CrO_3 + + Ti(i-OPr)$_4$ +. $(NH_4)_2SiF_6$ on silica; Cr = 0.4%, Ti 4.5%, F 0.3%	Bis(triphenylsilyl) chromate on silica-alumina support. A dialkylaluminum alkoxide is used as cocatalyst.
5. Density	0.91 — 0.93 g/cc	0.925 — 0.94 g/cc	0.94 — 0.96 g/cc
6. MFI	0.2 — 50	0.1 — 50	0.03 — 50
7. MFI Control	Use of chain-transfer agent (LPG gas)	Use of chain-transfer agent (H_2)	Use of chain transfer (H_2) varying the nature of alkoxy group in cocatalyst or varying the temperature
8. Structure	An average LDPE contains 50 short branches and 1 long branch as a result of inter and intra- molecular chain transfer reactions	Linear PE interspaced uniformly with short ethyl branches	Linear PE
9. Properties	—	Stiffer, superior low temperature brittleness and environmental stress crack resistance properties compared to conventional LDPE	Properties similar to Ziegler HDPE

TABLE II — ZIEGLER POLYPROPYLENE CATALYSTS — CONVENTIONAL SCENE

Feed = Propylene (+ butene-1)

Catalyst = Heterogeneous complex of organoaluminum compounds (R_3Al, R_2AlCl) with transition metal halides such as $TiCl_3$, $TiCl_2$, VCl_3, $CrCl_3$

Mode	**Conditions**	**Features**
1. High boiling solvent process (CSTR)	70°C/6.5 kg cm^{-2}	Efficient removal of tactic PP and catalyst; low catalyst activity; energy input required for solvent recovery.
2. Low boiling (monomer) solvent process (CSTR)	66°/26 kg cm^{-2}	Easy product separation by propylene flashing; high catalyst activity; difficult to remove atactic PP and catalyst residues; no solvent recovery.
3. Solution process (CSTR)	160—250°C/66 kg cm^{-2}	Easy removal of reaction heat and reduced residence time; difficult solvent handling and poor stereospecifity.
4. Gas phase process fluidised bed)	90°C/30—35 kg cm^{-2}	

UHMW-PE as a consequence of their high melt strength possess good parison stability and can be processed using high force techniques into large blow moulded articles such as industrial containers. The gas phase HDPE process possesses many advantages such as reduction in equipments, elimination of solvent handling and recycling, eliminating of extrusion--pelletization steps resulting in reduced capital and operating costs, energy savings and greater operational safety.

The alternative HDPE process is based on the Ziegler catalyst systems. In recent years, with the advent of the supported high activity catalysts, the technology has undergone substantial changes. Using specially formulated catalysts yields as high as 6000 kg. of polymer per gram of transition metal catalyst and a residual metal content of 2-10 ppm can be routinely achieved[5]. In addition the process offers substantial flexibility over the control of polydispersity. Possible reasons behind the high activity of these catalysts have been discussed previously[5]. These new processes offer significant capital and operating cost advantages as well as reduced investments in effluent treatment.

C. Polypropylene. The conventional technologies used in the Ziegler polymerization process are outlined in Table II. Table III presents a typical cost analysis of a polypropylene facility based on a high boiling solvent process. It is evident that elimination of steps 3(a-c) can result in substantial savings. The thrust of the second generation PP processes have been aimed in this direction. Conventional Ziegler catalysts produce as high as 10-12% atactic PP, yields only 3 kg. PP/g Ti and even after washing 300 ppm of catalyst is found in the product. Using monomer as solvent and employing new high activity catalysts based on titanium trichloride, and organomagnesium halide (n-BuMgCl/hexane) in conjunction with diethylaluminium chloride, steps 3(a-c) can be totally eliminated. Supported catalysts of the type used for HDPE modified with an electron donor compound (such as ethyl benzoate, tetramethylenediamine) have also met with limited success. However, the objectives of achieving high reaction rates without loss of stereospecifity have generally proved more difficult.

It is obvious from Table III that a major percentage of cost is involved in the extrusion-pelletization step. Third generation processes aimed at generating PP in a pellet configuration within the reactor itself by controlling particle morphologies during polymerization are in the stage of early evolution. Seen in this context, the discovery of a catalyst for the gas phase polymerization of propylene, capable of high activity and stereospecifity, will constitute a major process breakthrough. For it is already known that gas phase processes can produce polymers directly in a granule form, thus eliminating the extrusion-pelletisation steps.

D. High-Cis-Polybutadiene: Unlike the Ziegler polyolefin catalysts, polydiene catalysts produce polymers of high cis content (96-98%) with excellent efficiencies at low concentrations of transion metal catalyst. A summary of the existing Ziegler catalyst systems is presented in Table IV.

However, the need for producing essentially 100% high-cis-polybutadiene has not gone unrecognized. The effect of isomeric impurities on polybutadiene is to diminish the rate of strain-induced crystallization leading to low green strengths of rubber. The dynamic properties of the rubber is only a function of polymer microstructure whereas desirable mechanical properties in the vulcanizates can be obtained by optimal compounding. Sterically pure high-cis-tactic polydienes, upon compounding, can result in vulcanizates with a good balance of dynamic and mechanical properties.

Recently, a new class of catalyst involving actinides and lanthanides elements has been found to be

TABLE III — COST ANALYSIS OF A CONVENTIONAL POLYPROPYLENE PROCESS

Activity	Cost, % of Total	Possible solution to effect cost reduction
1. Catalyst	8	—
2. Polymerization	20	—
3. Post-Treatment	14	Eliminate solvent Increase stereospecifity
a. Solvent recovery		
b. Atactic PP Separation		
c. Catalyst washing, alcohol recovery and effluent treatment	8	Increase yield per unit weight of catalyst
4. Extrusion-Pelletization	34	Eliminate extrusion-pelletization step.
5. Infra-structure	16	—

TABLE IV — ZIEGLER CATALYSTS FOR POLYBUTADIENE‡

No. Transition Metal Compound	Organo-aluminium Compound	Company	Phase†	Al/TM	% Cis	Efficiency g/g. TM	Comments
1. TiI_4	Et_3Al	Phillips (1956)	Ht	3-6/1	90—95	1000—24000	—
2. $CoCl_2$ $CoSo_4$	Et_2AlCl	Montedison Goodrich-Gulf Shell (1958)	Ht	1-5/1	98	150—200	No need for additional activators
3. $Co(Oct)_2$ $CoCl_2$-Pyridine	Et_2AlCl	Phillips	Hm	100-1000/1	98	10^6	Water is needed as activator
4. π-Allyl Nickel halides	Et_2AlCl	Japan Synthetic Rubber Co. (1965)	Hm	—	97	10^3—10^4	—
5. Ce(Octoate)	EASQ	Union Carbide (1964)	Hm	18/1	99	3000	Cerium residues catalyzes oxidative degradation of rubber

‡ Solvent: Benzene † Ht: Heterogeneous, Hm: Homogeneous

promising in producing very high cis-polydienes[6]. Specifically, it has been disclosed[6a] that a Ziegler catalyst based on π-allyl uranium halides in conjunction with ethylaluminium dichloride can polymerize butadiene in extremely low uranium concentrations (Butadiene/uranium : 20,000) in n-hexane solvent to $> 99\%$ high-cis-polybutadiene at $+ 20°C$. The polymer has a broad molecular weight distribution ($Mw/Mn = 4$) and as anticipated possesses very short crystallization half times (Table V). These factors lead to improved mill processability, superior green strength and an optimum balance of dynamic and mechanical properties at low filler loadings because part of the necessary reinforcement is provided through crystallization when the rubber is stretched.

Unlike other Ziegler polybutadiene catalysts, the π-allyluranium catalysts can be used with aliphatic solvents. In view of the now accepted occupational health hazards of benzene, its replacement constitutes a major advantage of the new process. Furthermore, uranium is already a cheap material, obtainable as a byproduct of nuclear fuel cycles from the gaseous diffusion plants.

Another area, which is conspicuous by the absence of any reference to it in the literature, is the use of supported Ziegler catalysts for polydienes. It is possible that such modified catalysts can enable polybutadiene polymerization in non-aromatic solvents. Further, conventional Ziegler polydiene catalysts are limited by the fact that they can produce polymers of only one microstructure. Supported Ziegler catalysts may enable a continuous variation of stereochemistry as a function of support. In partial support of this hypothesis, it has been recently reported that π-allyl complexes of nickel supported on silica gives 96% cis-polybutadiene, while the same catalyst supported on alumina gives 98% trans-polybutaliene.

ULTRA-HIGH MODULUS THERMOPLASTICS BY POST-POLYMERIZATION TECHNIQUES

In spite of the many advantages of plastics in structural applications, their load bearing capacity is extremely poor, severely limiting their use in these applications. Isotropic modulus of commercial plastics are generally low ($\sim 10^9$ Nm^{-2}) and are compared with the modulus of some well known structural materials such as glass and steel in Table VI. In practice, modulus of a crystalline polymer can be increased by orientation or by providing reinforcements by high modulus materials such as glass fibre. In the latter approach, the cost doubles, fabricating costs increase and the density advantage is lost.

This discouraging situation would probably eliminate plastics from any consideration other than low stress bearing materials, if it were not for the fact that the ultimate theoretical modulus of crystalline polymers is about 10^{11} Nm^{-2}, of the same order as that of steel.

A deeper understanding of the molecular morphologies of crystalline thermoplastics have enabled a substantial increase in their modulus from their isotropic value[7]. HDPE (Mw 67,800) is cooled slowly (7-9°C/min) from 160°C to 110°C, and drawn on

TABLE V — CRYSTALLIZATION CHARACTERISTICS OF POLYBUTADIENE

Transition Metal catalyst	Cis %	$\tau\frac{1}{2}$ ᵃmin	Tm°C	X%ᵇ
Uranium	99	5	+2.2	40
Nickel	96-97	30	—1.0	35
Cobalt	96-97	40	—3.0	35
Titanium	92-94	900-5000	—8.0	25

ᵃ $\tau\frac{1}{2}$ half life of crystallization at a Tc = —20°

ᵇ % crystallinity

an Instron at 75°C at a crosshead speed of 6 cm/min to an ultimate draw ratio of 34 and a modulus of 6×10^{10} Nm^{-2}. Similarly PP is cooled from 220°C to room temperature at the rate of 0.3°C/min, drawn as before at 110°C to an ultimate draw ratio of 18 and a modulus of 1.8×10^{10} Nm^{-2}. It is believed that by controlled quenching of crystalline polymers from its melt and then orienting it to high draw ratios, an extended chain crystal morphology with fewer chain fold defects is obtained.

In spite of this, only 30% of the theoretical modulus of polyethylene, 39% of polypropylene and 61% of polyacetal has been so far attained. These high modulus thermoplastics possess the potential of acting as compatible reinforcing agents to low modulus materials without the disadvantages found with non-polymeric reinforcing agents such as glass fibres.

NEW DEVELOPMENT IN COUPLING AGENTS FOR FILLED THERMOPLASTICS

Composites based on a continuous polymer phase and a dispersed inorganic filler are finding increasing applications in recent years. Fillers provide the composite with cost advantages, reduced coefficient of expansion, improved tensile strength, modulus and heat distortion temperatures. They adversely affect processability by a reduction in melt flow, impact and elongation properties. The property changes are most pronounced with crystalline thermoplastics such as PP, HDPE etc., where polymer crystallinity reduces polymer mobility, providing more stable sites for polymer-filler interaction.

TABLE VI -- MODULUS VALUES OF SOME MATERIALS

Material	Condition	Modulus, Nm^{-2}
High density polyethylene	Isotropic	1×10^{9}
Poly(ethyleneterephthalate)	Fibre	1.4×10^{10}
Polypropylene	Theoretical	4.2×10^{10}
Polyacetal	Theoretical	5.4×10^{10}
Glass		7×10^{10}
Poly(ethylene terephthalate	Theoretical	1.2×10^{11}
Kevlar	Fibre	1.3×10^{11}
Steel	—	2×10^{11}
Graphite		$2.34 \times {}^{11}$
High density polyethylene	Theoretical	2.4×10^{11}
Poly(vinyl alcohol)	Theoretical	2.5×10^{11}

However, fillers are basically inorganic materials which possess no lasting adhesion to the organic polymer. In order to promote this adhesion, a coupling agent is normally used along with the polymer and filler. The most conventional coupling agents used with glass, silica, talc and magnesia are the organosilanes.[8] However the organosilances are non receptive to metallic fiber surfaces, hydrated amphoteric oxides and calcium carbonates.

Recently a new class of coupling agents based on organotitanates have been introduced which fill this gap in technology[9]. Additionally, organotitanate coupled filled polymer composites exhibit certain remarkable property improvements such as improved flow even at high filler loadings, enhancement of impact properties and compatibility with hydrated fillers such as alumina trihydrate, for example, untreated calcium carbonate and alumina trihydrate dispersed in mineral oil show a no flow characteristic at 45% loading. However, addition of 0.5% organotitanate enables one to maintain flow with no increase in viscosity till 70% loading.

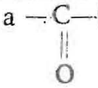
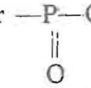
The various titanate types and their typical structures are illustrated in Chart II. In general they are characterized by a mono-functional titanium isopropropoxy group and a long aliphatic chain linked to the titanium via a  $-\underset{\underset{O}{\|}}{C}-O-$ bond or  $-\underset{\underset{O}{\|}}{P}-O-$ bond. The hydroxy groups on fillers react with the isopropoxy group on titanium resulting in the formation of Ti-O— Filler bond. Unlike the organosilanes which can enter into multifunctional bonding with the fillers, titanates form only monofunctional bonds. This is believed to be the cause of the desirable

TABLE VII -- EFFECT OF TITANATE ON $CaCO_3$ FILLED POLYPROPYLENE

% $CaCO_3$	%TTS	Flx. Modulus, psi	Impact Ft.lbs	MFI
0	0	240,000	1.0	5.0
70	0	550,000	1.5	0.0
70	3	380,000	7.5	4.70

TTS: Isopropyl triisostearoyl Titanate

CHART II
TYPES OF TITANATES

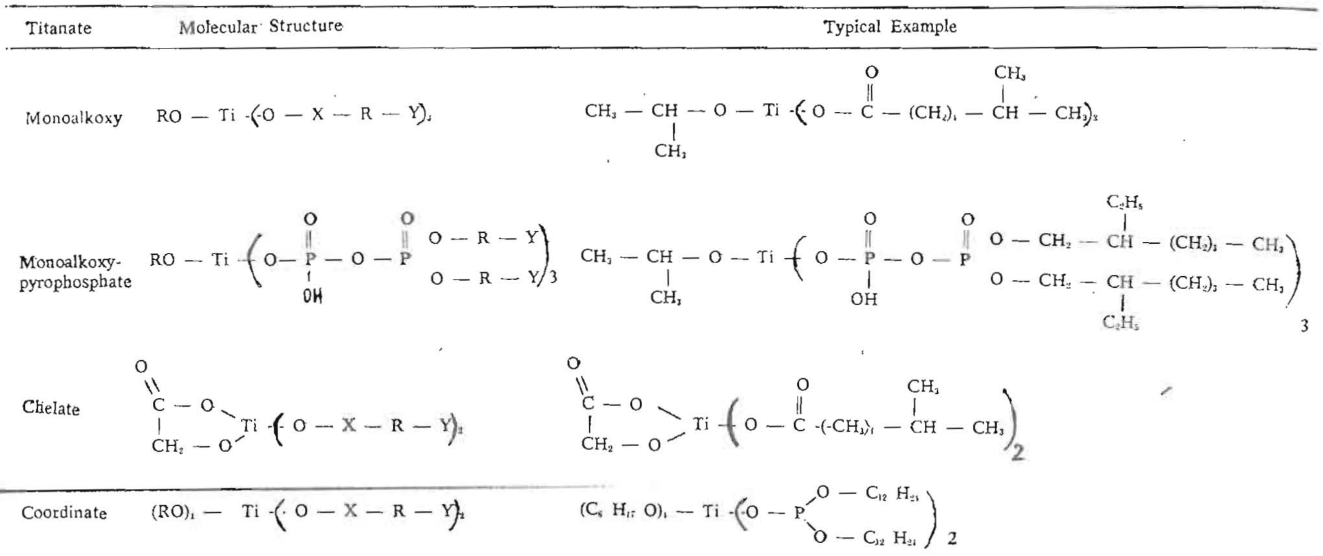


TABLE VIII — EFFECT OF TITANATES ON CaCO$_3$ FILLLED LDPE

Properties	LDPE	NO TTS	1% TTS	2% TTS	3% TTS
Tensile Strength, psi	1638	1464	1245	1222	1124
Modulus, psi	1204	—	—	—	964
Elongation, %	530	40	80	150	420

TABLE IX — TiO$_2$ DISPERSIBILITY IN LDPE WITH VARYING AMOUNTS OF TTS

TiO$_2$ 75%
TTS 0—4%
LDPE 21—25%
Mixing Temperature 200°C

%TTS	Torque Reagings after 180 sec. mixing	MFI
0	1100	0.00
1	1100	0.72
2	800	2,20
3	750	3.10
4	700	3.20

rheological properties which titanate treated fillers impart to filled plastics.

The effect of titanates in calcium carbonate filled polypropylene is to enhance melt flow and dramatically improve impact properties well above even virgin polypropylene (Table VII). The flexural modulus of 70% filled PP is higher than virgin polypropylene. One therefore has a unique situation where two opposing properties, namely impact strength and rigidity, are both enhanced simultaneously. The ability of titanates to improve elongation of 40% CaCO$_3$ filled LDPE is shown in Table VIII. In general, addition of filler causes an increase in the energy of processing. The ability of titanates to lower the energy required for mixing of 75% TiO$_2$ with LDPE is shown in Table IX. This results in other benefits such as faster extrusion, shorter cycle time, improved dispersion and reduced machine and die wear. In the extrusion of polypropylene filled with 50% CaCO$_3$, it was found that addition of 0.5 p.h.r. of titanate permitted a 100°F reduction in barrel temperature (to 300°F) with no change in torque of mixing.

Organotitanate coupling technology is generally applicable to thermoplastics (LDPE, HDPE, PP, PVC and polystyrene, thermosets (epoxies, unsaturated polyesters etc.) and elastomers (nitrile, EPDM, SBR etc.). With elastomers titanates improve filler dispersion and physical properties.

The precise mechanism by which oryanotitanates confer these property advantages in polymers is still uncertain It is believed that when an inorganic filler is treated with a titanate, it is converted to a filler with organic appendages that result in the following filler property changes: a) organophilic and hydrophobic than organophobic and hydrophilic; b) improved compatibility and dispersion; c) availability of filler organic appendages to mix with the polymer matrix and provide a molecular bridge for the transfer of stress energy from the polymer matrix to the filler phase without bond rupture in thermoplastic polymers ; d) ability of the filler organic appendages to enter into a chemical crosslinking with thermoset polymers. These factors coupled with their ability to enter into monofunctional bonding with fillers contribute to the desirable effects of the orgonotitanate coupling agent in filled polymer composites.

CONCLUSION

It is evident from the foregoing discussion that recent developments in polymers have been no less spectacular than in the previous two eras that this technology has witnessed during the past half century, namely that of the free science period of the fortys which laid the scientific foundation and the market led new polymer development period of the fiftys and sixtys. However, the evolving technologies of the seventies reflect the altered needs of the present time. This has in turn led to a greater fundamental understanding of the behaviour of polymeric materials and the science of polymers, in general, has been considerably enriched.

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DISCUSSION

Q: *How the entanglement density is taken into account in rubber reinforcement by carbon black ?*

A: The answer to this may be found in the following two references (a) Carbon Black - Physics, Chemistry and Elastomer Reinforcement, J.B. Donnet and A. Voet, Marcel Dekker, Inc., Ch, 8, 1976. (b) W.W. Graessley, Adv. Polymer Science, 16, 1 (1974)

Q: *Can the titanate coupling agents be applied to thermosets also ?*

A: The titanate coupling agents are generally applicable to thermoplastics, thermosets and elastomers. As in thermoplastics, they contribute to improved impact strengths and better melt flow of filled thermosets. In addition, specific interaction of the titanates with the carboxyl groups in unsaturated polyesters cause a transesterification reaction to occur. This establishes a chemical bond between the filler and the polymer resulting in a number of desirable properties. Similar reaction of the titanates with the OH-groups in epoxy resin is also possible which results in improved physical properties even at high filler loadings. Titanates can also be used to enhance the properties of $CaCO_3$ and clay filled Hypalon, clay filled EPR, HAF black filled SBR and clay/, black filled nitrile rubber.