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Chemical modification and blending of polymers in an extruder reactor

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Abstract. Chemical modification and blending of polymers in an extruder reactor are discussed. Relationships between the parameters affecting the reaction kinetics, *viz*., mixing time, duration of a chemical reaction and the residence time of the system in the extruder reactor, and the structure of the materials produced are analysed. The mechanisms of (i) grafting of low-molecular-mass compounds onto polymers; (ii) reactions between terminal groups of different polymers and (iii) transesterification and interchange reactions are considered. The factors affecting the mechanism of dynamic vulcanisation and the properties of thermoplastic elastomers are identified. Solid-phase reactions of polysaccharides in an extruder are discussed. The priority aspects of studies on the chemical modification and blending of polymers are noted. The bibliography includes 90 references.

I. Introduction

Polymeric composites are currently widely used and actively studied. Particular interest has been shown in multicomponent polymer blends and alloys. The creation of such polymeric materials entails the possibility of combining attractive qualities of each component of the polymer blend in the end product.[1–3] Useful properties of polymer blends are affected by such characteristics as the nature of the dispersed and dispersion phases, the volume ratio of the phases, the sizes and size distributions of the particles of the dispersed phase, and interfacial adhesion.

Much attention is paid by investigators to the processes of preparation of materials by blending components in which chemical reactions proceed.[4,5] Such processes are called 'reactive blending' or 'reactive extrusion'. Only a few polymers are thermodynamically compatible and form blends with homogeneous morphology at a molecular level. The majority of polymers exhibit limited compatibility or are incompatible and their blends possess heterogeneous morphologies.

Reactive blending extends the possibilities of controlling the phase structures of multicomponent polymeric materials. Not only does the technology for reactive blending of polymers open new ways for the employment of polymeric products already available but also permits the creation of blends, the preparation of which by other methods has been economically unfavourable. Application of methods of organic chemistry and reactive blending allows preparation of diverse modified polymers and polymer blends based on a a small number of industrially produced polymers.[4]

II. Characteristic features of reactive blending processes

1. Blending condition

Blending of polymers is an intricate physicochemical process, which proceeds under the action of mechanical and temperature fields. If blending of polymers is accompanied by chemical reactions, their rates are determined by the character of blending, temperature gradients and by diffusion of the reagents and products. These characteristics can be controlled if reactive blending is carried out in extruder reactors.

Currently, continuous extruder reactors (Fig. 1) are available. Extrusion is used for the preparation of products or semifinished items of desired shape by forcing polymer melts through an exit (a shape-forming orifice).[6–8] Extrusion processing of plastics is effected by using mainly single-screw and twin-screw extruders. Technologies with employment of extruder reactors combine the processes that are usually separated, *e.g*., blending, chemical reactions and moulding. Here, new problems arise associated with, *e.g*., changes in the viscosity during the reaction or heat removal. Some lines of attacking such problems, as applied to polymerisation reactions, have been considered.[5,9] It was found that in the case of chemically reacting systems twin-screw extruders are preferable to single-screw extruders owing to more efficient mixing and heat removal. However, the complexity of chemical and physical processes proceeding in an extruder reactor hampers the choice of the moulding parameters and equipment.

This requires experimental and theoretical studies on the evolution of the structure and properties of polymers during the preparation of materials using extruder reactors.[10–13] However, experimental investigation of the polymer structure is a complicated multiparameter problem. On the other hand, only a few

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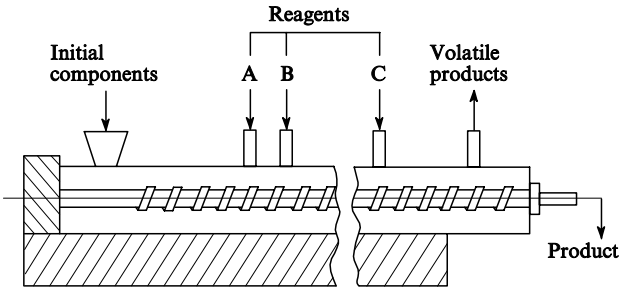


Figure 1. A scheme of an extruder reactor.

theories which allow qualitative description of the changes in the polymer structures after completion of the chemical reactions in the system have been developed.[14–16] This can be illustrated as follows. If a reaction proceeds in the melt, the reaction rate can be strongly affected by diffusion. Changes in the blend composition during the reaction can in turn affect the diffusion processes. Therefore, a theory is required which describes the evolution of the structure of a polymer blend taking into account the mutual influence of the chemical reaction and diffusion.[17]

Changes in the structure of a model heterogeneous blend, in which the copolymer AB is an intermediate of a polymeranalogous reaction A → B have been considered.[18] It was shown that diffusional mixing has a pronounced effect on the reaction kinetics. This effect manifests itself if the characteristic time of the chemical reaction,

$$\tau_r = \frac{1}{k},$$

(k is the rate constant of the chemical reaction) is shorter than, or comparable with, the mixing time τ_m. The mixing can be considered efficient if

$$\tau_m < \tau_r. \qquad (1)$$

This condition holds well for the alcoholysis of poly(ethylene-*co*-vinyl acetate) with aliphatic alcohols (octan-1-ol, 2-ethylhexan-1-ol, 3-phenylpropan-1-ol) in the bulk and in solution (dodecan-1-ol) with dibutyltin dilaurate as catalyst.[19] The bulk reaction was carried out in a Haake Rheochord mixer (Germany).

It was shown [19] that the reaction in solution and in the bulk follows the same mechanism, which is independent of the nature of the alcohol. The equilibrium constants of the reactions in solution and in the bulk were equal. The reaction rates were of the second order with respect to the concentrations of reagents. The viscosities of the systems in solution and in the bulk differed by five orders of magnitude. Based on the results of analysis of the kinetic data, it was suggested that (i) the reaction rate is substantially lower than the diffusion rate and (ii) mechanical mixing is necessary only for the homogenisation of the reaction system in the initial stage of the reaction (once this is achieved, mixing is of no significance during the reaction).

However, the differences between the limiting degrees of conversion have not been discussed.[19] From the plots reported in this study it follows that the limiting degree of conversion in the bulk at 180 °C is ~65% while that in solution at 170 °C is ~90%. This is most likely due to the change in the viscosity of the reaction system.

Usually, the viscosity of the medium increases during the reaction, thus hampering homogenisation of the reaction system and leading to the formation of structurally inhomogeneous material. Changes in the viscosity during the ionic and radical polymerisation reactions have been analysed [9, 20] and a theoretical approach to quantitative estimation of these changes has been considered.

During the reaction, the system can become heterogeneous and the reaction kinetics can in turn change. The kinetics of the chemical reactions in homogeneous and heterogeneous polymer melts have been analysed taking the esterification reaction between 1-naphthylacetic acid (NAA) and a random ethylene/ethyl acrylate/glycidyl methacrylate (E–EA–GMA) terpolymer as an example.[21] Being initially homogeneous, the system NAA–E–EA–GMA became heterogeneous upon addition of an inert polymer, *viz*., polystyrene (PS). Polystyrene and E–EA–GMA are immiscible, whereas NAA can be mixed with both polymers in the concentration and temperature ranges studied. It was shown that the mechanisms of these reactions are identical and that the rate of NAA diffusion is much higher than the reaction rates in both systems.

Thus, preparation of materials with homogeneous distribution of submicroscopic particles of the dispersed phase requires that the condition (1) be met.

2. Effect of the residence time of a system in an extruder reactor

The reaction in an extruder reactor goes to completion if

$$\tau_r \ll \tau_f, \qquad (2)$$

where τ_f is the mean residence time of the reaction system in the extruder reactor (hereafter, the residence time). This time depends on the ratio of the extruder length, l, to the longitudinal component of the flow rate, V,

$$\tau_f = \frac{l}{V}. \qquad (3)$$

Generally, the residence time is determined by some distribution function.[22] The distribution functions, f(τ), for a ZSK-30 co-rotating twin-screw extruder (Werner and Pfleiderer, Germany; screw length-to-diameter ratio, $l/d = 42$) are shown in Fig. 2*a*. Proceeding to the dimensionless time

$$\theta = \frac{\tau}{\tau_f},$$

where τ is the current residence time of the reaction system in the extruder reactor, gives the residence time distribution function, f(θ), shown in Fig. 2*b*. As can be seen, the f(θ) curves are shifted to a short-time domain when the feed rate Q and screw speed N increase, *i.e*., τ_f shortens and the f(θ) curves match one another. It is believed that the mechanical mixing intensity does not vary much upon varying Q and N at a constant Q/N ratio. On the other hand, the residence time distribution function, which characterises macromixing, changes. The ratio between the convection mass transfer in a flow and free molecule diffusion is characterised by the Peclet number (criterion), Pe (Ref. 24)

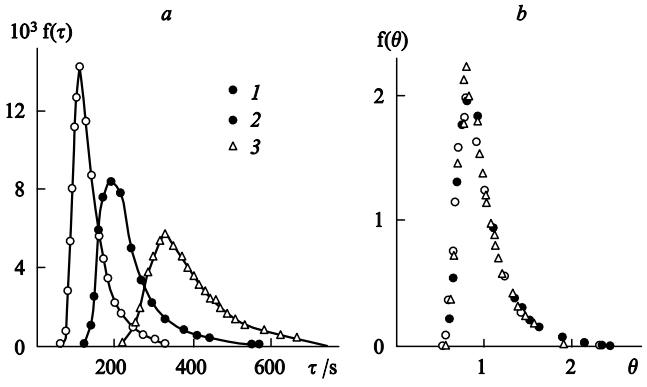


Figure 2. Residence time distribution function in dimensional (*a*) and dimensionless form (*b*) as a function of the feed rate Q and screw speed N at a constant Q/N value of 1/43 kg min h^{-1} rev^{-1};
(*1*) Q = 5.6 kg h^{-1}, N = 240 rev min^{-1}; (*2*) Q = 3.5 kg h^{-1}, N = 150 rev min^{-1}; (*3*) Q = 2.1 kg h^{-1}, N = 90 rev min^{-1}.[24]

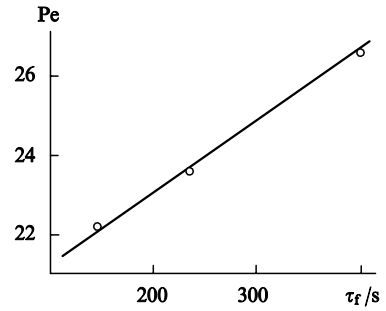


Figure 3. Dependence of the Peclet number on the residence time.

$$\mathrm{Pe} = \frac{Vl}{D},$$

where D is the diffusion coefficient. The dependence of the Peclet number on τ_f is shown in Fig. 3. As can be seen, the Pe number increases as τ_f increases. This plot was constructed using the results obtained by Sun *et al.*[23] Unfortunately, they reported no numerical data for the calculation of the Peclet numbers. At small Pe values, free molecule diffusion predominates, while convection mass transfer is predominant at large Pe values. Hence, the contribution of the convection mass transfer increases with lengthening of the residence time τ_f, (*i.e.*, with a decrease in the feed rate Q and screw speed N).

The residence time was found to be the main parameter which controls the degree of grafting (q) of, *e.g.*, GMA onto polypropylene (PP). As Q and N decrease, τ_f and q (Fig. 4) increase. On the other hand, the degree of grafting decreases with increase in the energy supplied per unit mass of the reacting system U (Fig. 5).

Thus, the degree of grafting is mainly determined by the mixing mechanism rather than energy expenditure.

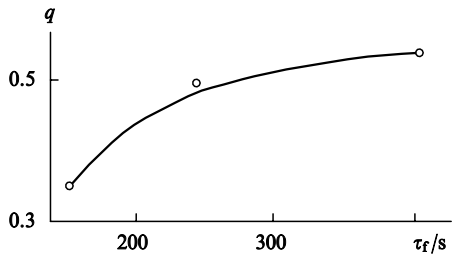


Figure 4. Dependence of the degree of grafting of GMA onto PP (q) on the residence time at $l/d = 42$, $Q/N = 1/43$ kg min h^{-1} rev^{-1}.

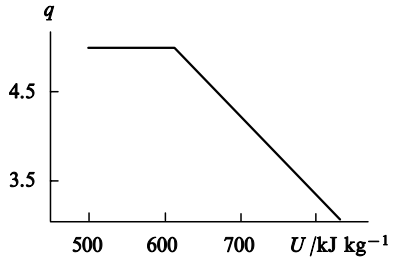


Figure 5. Dependence of the degree of grafting on the energy supplied per unit mass of the reaction system at $Q/N = 1/43$ kg min h^{-1} rev^{-1} (see Ref. 24).

III. Grafting of low-molecular-mass compounds onto polymers

1. Grafting onto polypropylene

Modification of polymers is carried out for compatibilisation of polymer blends. This is achieved by using block and graft copolymers.[25] Preparation of diverse polymer blends by reactive blending has been reported.[4] The synthesis of graft copolymers of polyalkenes by reactive extrusion has been reviewed[26] and the mechanisms of grafting and structures of graft copolymers depending on the reaction conditions have been analysed.

Polypropylene is one of the intensively studied polymers. Grafting of GMA onto PP proceeds by a radical mechanism. The limiting degree of grafting increases with increase in the peroxide concentration[23] as well as upon introduction of styrene as the second monomer. In the latter case, $\overline{M}_w$ increases from 220 000 in the absence of styrene to 350 000 in the presence of styrene.

The stage that follows grafting is blending of polymers. Here, reactions of graft polymers with other blend components take place. These reactions result in improvement of interfacial adhesion. Problems arising where two processes, *viz.*, functionalisation and chemical mixing, are carried out in one extrusion step have been considered.[27,28]

In situ compatibilisation of PP and poly(butylene terephthalate) (PBT) blends (PP : PBT = 70 : 30) was carried out by one-step reactive extrusion in a ZSK-30 co-rotating twin-screw extruder (Werner and Pfleiderer, Germany) ($d = 30$ mm, $l/d = 42$).[27] Possible screw configurations are schematically represented in Fig. 6.[28] The extruder is divided into two functional zones: grafting of GMA onto PP is carried out in the first part of the extruder and the reaction between the GMA-*g*-PP and the carboxy group of the PBT is carried out in the second part of the extruder.

It was found that changes in the compatibility of the PP – PBT blend are accompanied by changes in its morphology. In the mechanical blend of the initial components, the particle size of the dispersed phase (PBT) was larger than in the blend of grafted PP and PBT. In the latter case, the interfacial adhesion was also improved.

The plot of the residence time distribution function in the reaction of PP with PBT[27] is similar to that considered above (see Fig. 2 *a*). As the feed rate Q and screw speed N increase, the residence time distribution function curve is shifted to the short-

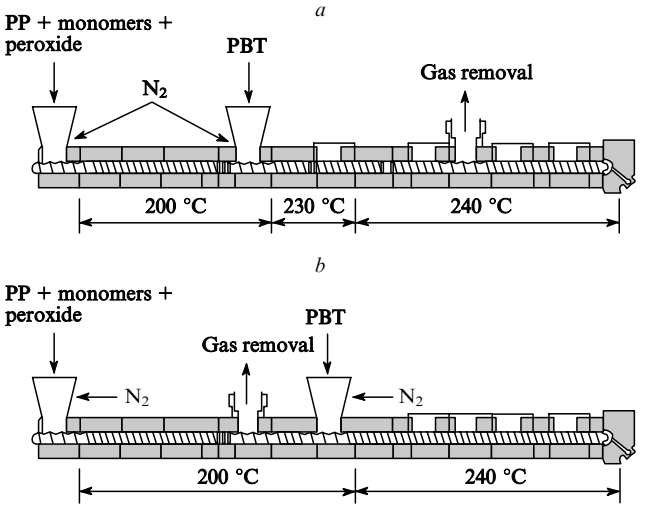


Figure 6. Examples of screw configurations for combining the modification of PP and its blending with PBT.[28]

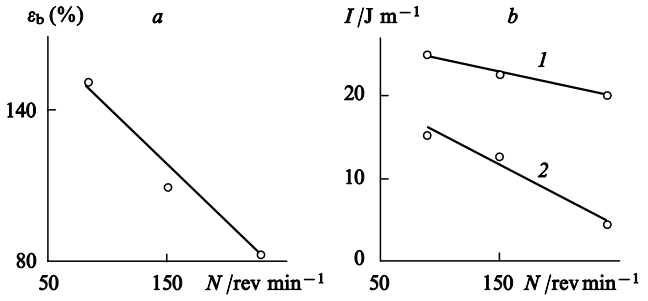


Figure 7. Dependence of the elongation at break (*a*) and impact strength (*b*) on the screw speed at $Q/N = 1/30$ kg min h^{-1} rev^{-1} (see Ref. 27). Temperature: (*1*) 0 and (*2*) 720 °C.

time domain. In dimensionless coordinates, the plots of these functions match one another (see Fig. 2*b*).[24] The elongation at break and the impact strength depend on the residence time of the system in the extruder. With a decrease in Q and N, the residence time lengthens and, correspondingly, the elongation at break (ε_b) and the impact strength (I) increase (Fig. 7).

The effects of the chemical nature and concentration of compounds subject to grafting onto PP, the concentration of the initiator (peroxide) and some other parameters on PP modification have been studied.[28] Among the three compounds studied, namely, acrylic acid (AA), maleic anhydride (MA) and GMA, the last-named compound was found to be the most efficient for the modification of PP–PBT blends. After optimisation of the reaction conditions, the elongation at break and impact strength of the modified PP–PBT blend (PP : PBT = 70 : 30) increased 15- to 20-fold as compared with the corresponding parameters for the mechanical blend. Further increase in the PBT concentration leads to a decrease in the elongation at break and impact strength of the modified PP–PBT blend. This is probably due to cross-linking reactions.

Comparison of the properties of the polymer blends prepared by one-step reactive extrusion[27] and by conventional two-step technique showed that the elongations at break and impact strengths of the blends prepared by the former method are higher.[8]

Numerous studies have been concerned with grafting of MA onto PP.[29–34] It was shown[29] that if the reaction was carried out with 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane as the initiator, the dependence of the degree of grafting on the MA concentration passes through a maximum. This is due to the fact that the PP–MA system becomes a two-phase system with an increase in the MA concentration and, hence, the effective concentrations of the MA and peroxide decrease. In this case, the grafting reaction was carried out in a batch mixer at 215–220 °C at a rotor speed of 64 rev min^{-1} over a period of 15 min. If grafting is carried out in a twin-screw extruder (200 °C, $\tau_f = 3$ min, screw speed = 75 rev min^{-1}), the degree of grafting increases; however, intense degradation of the extrudate is observed.

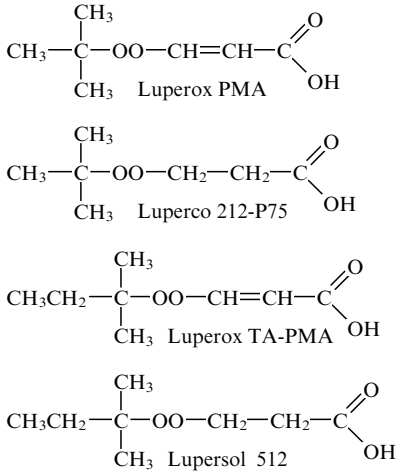
Modification of PP is accompanied by its degradation. An important problem is to reduce the degree of polymer degradation during the grafting. It was found[23] that introduction of an electron-donor monomer (*e.g.*, styrene) causes an increase in the degree of grafting of MA onto PP and substantially inhibits degradation.

Similar results were obtained by Bettini and Agnelli[30,31] who studied the effect of content of MA and a 46.5% concentrate of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane in $CaCO_3$, the rotor speed and duration of the reaction on the degree of grafting of MA onto PP and on changes in the molecular mass (MM). Blending was carried out in a System 90 torque rheometer (Haake, Germany) equipped with a Rheomix 600 mixer. It was found that an increase in the peroxide concentration leads to an increase in the degree of grafting and to a decrease in the MM. The dependence of the degree of grafting on the MA concentration passes through a maximum, the position of which is determined by the rotor speed and duration of the reaction. Degradation of PP is a complex function of the MA concentration: at high MA concentration, the melt flow index (MFI) decreases, *i.e.*, the degradation of PP is retarded.

Grafting of MA onto PP of different stereoregularity in melt and in solution in the presence of dicumyl peroxide has been compared.[32–34] Similarly to the reactions discussed above, the dependence of the degree of grafting on the MA and peroxide concentrations was also found to pass through an extremum. The degree of grafting in the melt was higher than that in solution (with xylene and decalin as solvents). The maximum degree of grafting onto atactic PP was found to be higher than onto isotactic PP. However, the modified atactic PP was more compositionally heterogeneous.

Different types of peroxides were used as radical initiators of the grafting reactions. Naturally, the question arises: how does the chemical nature of the peroxide affect the grafting kinetics?

A number of functional peroxides (peroxy esters) has been studied.[35] The structures of functional nonsymmetric peroxides and the corresponding trade names are shown below.



Blending of PP and peroxides was carried out in a Rheochord 90 counter-rotating, twin-screw extruder (Haake, Germany). The screw speed was 15 rev min^{-1}, which corresponded to a residence time of ~ 7 min. The reactions were carried out in a N_2 atmosphere. It was assumed that the residence time is sufficient for the peroxides to decompose completely.

The degree of grafting of a carboxylic acid onto PP and degradation of PP has been studied.[35] Grafting reactions carried out in the presence of peroxides which decompose to give methyl radicals were found to be more efficient than those in the presence of peroxides which decompose to give ethyl radicals. The increase in the concentration of polymeric radicals leads to an increase in the degree of grafting and to greater degradation of PP. A similar effect was also observed upon the formation of radicals with double bonds.

Thus, varying the molecular structure of the peroxide allows the degree of grafting of functional groups onto PP to be changed.

Grafting of MA onto PP can also be carried out using not only radical reactions accompanied by intense degradation of PP but also other types of reactions. The degradation upon radical modification of PP can be reduced and the process becomes controllable if a 'specific' functionalisation, *viz.*, the reaction of the terminal vinylidene groups with various compounds, is carried out. Among possible reactions, the Alder ene addition seems to be the most convenient to be performed in an extruder reactor.[36] The reaction rate depends on the acidity and basicity of the ene moiety and enophilic fragments and on the reaction conditions; it increases in the presence of Lewis acids.

Grafting of MA onto PP in the presence of Lewis acids ($SnCl_2$, $RuCl_2$) in an LSM 30.34 co-rotating twin-screw extruder (Leistritz, Germany; $d = 34$ mm; $l/d = 42$) has been studied.[36]

Grafting of MA onto PP using the Alder ene reaction was shown [36] to proceed without considerable degradation of PP. An increase in the reaction temperature and the MA concentration leads to an increase in the degree of grafting, which also increases with improved mixing. For this reaction, $RuCl_2$ was found to be a more efficient catalyst than $SnCl_2$.

2. Grafting onto polyethylene

Polyethylene (PE) is yet another polymer which is widely used in polymer blends. The number of different types of PE is larger than that of PP. Therefore, it is of interest to analyse the effect of grafting onto PE as function of its structure. Grafting of diethyl maleate (DEM) onto high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) in two co-rotating twin-screw extruders, namely, a ZSK-30 extruder (Werner and Pfleiderer, Germany) and a ECS-2E25 extruder (Berstorff, Germany) has been studied.[37] Screw configurations, extrusion conditions and the order of introduction of the components into the extruder were varied. The effects of different parameters on the residence time distribution function were analysed. As for PP, the efficiency of grafting was determined by the residence time. When the transport delay time and the mean residence time exceeded certain critical values, the concentration of free radicals decreased owing to secondary reactions (*e.g.*, thermal oxidation, mechanochemical degradation and/or chain branching, *i.e.*, the formation of long branches for LLDPE), which resulted in a decrease in the degree of grafting.

An increase in the degree of grafting with increase in the initiator concentration was independent of the screw configuration and extruder type. The molecular mass distribution (MMD) of the DEM graft LLDPE was virtually the same as that of the initial sample. However, $\bar{M}_w$ of the DEM graft HDPE decreased and the MMD became narrower. Hence, the degree of grafting onto PE is determined by the residence time of the system in the extruder while the MMD is determined by the type of the PE.

Rosales *et al.*[37] also studied the influence of chemical nature of the peroxide by comparing the effects of a 90% solution of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane and dicumyl peroxide. The second initiator was found to be less efficient.

A study of the effect of the degree of grafting on the rheological and thermal properties has been reported.[38] It was shown that the rheological properties are more sensitive to the changes due to grafting than the structural parameters determined from the measurements of thermal behaviour. An increase in the dynamic viscosity with increase in the degree of grafting was observed at low frequencies of strain sweep. Mention was made that the blends obtained possess enhanced compatibility with polyamides and polyesters.

Compared to the molecular structure characteristics, the rheological properties of the modified LLDPE are also more sensitive to the changes due to reactions at low peroxide concentrations.[39, 40] LLDPE was extruded in the presence of the initiator, 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane, in a co-rotating twin-screw extruder (Leistritz, Germany; $d = 34$ mm, $l/d = 35$). The screw configuration was varied. The peroxide concentration was low in order to prevent cross-linking. In this case, the MMD broadened owing to an increase in the percentage of the high-molecular-mass fraction, which increased with increase in the peroxide concentration.

The proportion and lengths of the side groups were determined by different methods (size-exclusion liquid chromatography, nuclear magnetic resonance, differential scanning calorimetry). It was found that the proportion of unsaturated terminal units in the modified LLDPE diminished. Based on the results obtained, a reaction mechanism was proposed.

The authors established that an increase in the complex viscosity at low frequencies of strain sweep is due to the formation of a small number of long-chain branches. Changes in the molecular parameters of the modified LLDPE affected not only the shear characteristics of the flow but also the flow characteristics in the longitudinal direction. The modified LLDPE had higher viscosity in the longitudinal direction. However, this was accompanied by a decrease in the tensile deformability. Swelling of the extrudate decreased with increase in the peroxide concentration. The efficiency of the LLDPE modification in the extrusion strongly depended on the temperature and quality of mixing.

The influence of extrusion on the cross-linking and degradation of PE has been studied.[41] Cross-linking of HDPE in the presence of a peroxide, 1,3-bis(*tert*-butylperoxyisopropyl)benzene (system 1), and mixtures of this peroxide with coagents, *viz.*, trimethylolpropane triacrylate (TMPTA) (system 2) and *para*-benzoquinone (PBQ) (system 3), in the extrusion in a twin-screw extruder ($d = 25$ mm; $l/d = 30$) at 230 °C has been studied.

It was shown that the MFI decreased rapidly as the peroxide concentration increased in system 1, more smoothly in system 2 and showed a slight increase in system 3. The last-named effect was probably due to degradation of HDPE.

Thermal properties of the modified HDPE depend on the peroxide concentration in a complex manner. The melting temperature, T_m, and the crystallisation temperature, T_{cr}, increase with increase in the peroxide concentration. On the other hand, T_m decreases while T_{cr} increases as the concentration of the peroxide–TMPTA initiator increases. Initially, the heat of melting increases and then decreases with increase in the concentration of the initiator.

The effect of the peroxide and TMPTA concentrations on the mechanical properties can be followed from the data listed in Table 1. As can be seen, the impact strength increases by ~ 7-fold as compared to that of the initial HDPE.

Table 1. The effect of the peroxide and TMPTA concentrations on the mechanical properties of cross-linked HDPE.

[Peroxide] [a]	[TMPTA] [a]	MFI /g/10 min	D	I	E	σ_y	ε_b
–	–	4.74	61	148	1290	27.5	600
0.05	–	1.62	62	576	1290	30.0	20
–	0.3	0.95	62	1084	1400	37.5	30
0.05	0.3	0.037	64	770	1440	42.0	30
0.01	0.1	1.78	62	908	1340	35.0	30
0.01	0.2	0.98	63	1032	1410	39.0	20
0.02	0.1	0.49	61	1011	1340	35.5	20
0.02	0.2	0.13	62	1016	1420	38.5	20

Note. The following notations are used here and in Tables 2–5: D is the hardness (arbitrary units), I is the notched Izod impact strength (J m^{-1}), E is the flexural modulus (MPa), σ_y is the yield stress (MPa) and ε_b is the elongation at break (%).

[a] The concentrations of peroxide and TMPTA are given in mass parts per 100 mass parts of HDPE.

3. Grafting onto an ethylene/propylene terpolymer and polylactide

Grafting of MA onto ethylene/propylene/ethylidenenorbornene terpolymer (EPDM, with ethylene and ethylidenenorbornene concentrations of 56 mass % and 5.7 mass %, respectively) in a Rheomix 750 mixer (Haake-Buchler, Germany) at ~ 160 °C with dicumyl peroxide as the initiator has been studied.[42] It was shown that the amount of the gel fraction initially increases up to 4 mass % with an increase in the MA concentration and then decreases. On the other hand, the amount of the gel fraction increases monotonically with increase in the peroxide concentration.

As in the case of polyalkenes, the dependence of the degree of grafting onto EPDM on the MA concentration increases as the MA concentration increases up to 3 mass % and then decreases, thus passing through an extremum. The degree of grafting

increases with increase in the peroxide concentration. The reaction is accompanied by cross-linking and degradation of the terpolymer.

Introduction of an electron donor (*e.g.*, stearamide) into the reaction system inhibits side reactions, *viz.*, cross-linking and degradation. The optimum content of stearamide was found to be ~ 20 mass %.

Grafting of MA onto other types of polymers has also been studied. In particular, a study on the grafting of MA onto polylactide in a co-rotating twin-screw extruder (Baker Perkins, United Kingdom) with 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)-hexane as the initiator has been reported.[43] Polylactide is a biodegradable polymer widely used in medicine. It was shown that the degree of grafting increases with increase in the initiator concentration, while MM decreases (the MFI increases). The ratio of the weight-average molecular mass to the number-average molecular mass, $\bar{M}_w/\bar{M}_n$, remained virtually constant. It was found that even a small amount of the MA graft onto polylactide essentially improves the interfacial adhesion in the polylactide-based blends and composites.

IV. Reactions between terminal groups of polymers

Chain extension in PBT owing to the reactions of the epoxy groups of diglycidyl tetrahydrophthalate with the terminal hydroxy and carboxy groups of PBT has been studied.[44]

The synthesis of high-molecular-mass PBT is a rather complicated problem. Industrially, PBT with an MFI greater than 20 g/10 min can be produced, while the PBT with relatively low MM possesses poor mechanical properties. Therefore, the problem of chain extension is topical. One of the possible ways of solving this problem is to carry out reactions of bifunctional compounds with terminal groups of PBT. Guo and Chan[44] carried out the reaction of epoxy groups with the carboxy and hydroxy groups of PBT in a Rheomix 600 mixer (Haake, Germany). The rotor speed was varied from 30 to 120 rev min^{-1} and the temperature was varied from 230 to 280 °C. As the temperature was raised and the rate of shear increased, the duration of the reaction of the terminal groups of PBT with the epoxy groups decreased owing to an increase in the rate of diffusion of the epoxy groups. The duration of the reaction was found to be ~ 3 min at 260 °C. Therefore, this reaction can be performed in both single-screw and twin-screw extruders.

The results of mechanical and rheological tests of the PBT thus obtained are listed in Table 2. As can be seen, the MFI value decreases rapidly with increase in the concentration of epoxy groups, while the notched Izod impact strength and the elongation at break increase. The PBT thus obtained was found to be more thermally stable.

Table 2. The effect of the concentration of epoxy groups [E] on the mechanical properties of PBT.[41]

[E] (mass %)	σ_b /MPa	ε (%)	σ_{bn} /MPA	I /J m^{-1}	MFI /g/10 min
0	53.7	50.2	88.6	19.9	35.4
0.4	54.4	62.3	91.2	20.2	29.8
0.5	53.9	76.9	91.7	22.9	23.5
0.7	52.3	101.8	93.2	23.2	17.8
0.8	52.6	130.4	89.3	24.1	15.4
0.9	52.3	267.7	93.3	25.7	13.1
1.0	53.5	262.5	92.1	26.3	10.3
1.2	53.0	278.5	92.5	34.4	8.4
1.3	53.0	329.2	93.0	39.2	5.0
1.4	52.9	360.1	92.4	51.9	3.6
1.6	52.1	360.0	92.2	49.5	2.6

Note. The following notations are used: σ_b is the tensile strength and σ_{bn} is the bending strength.

On the other hand, the reaction considered above can be accompanied by cross-linking; the longer the chain the higher the degree of cross-linking. Cross-linking begins as the concentration of epoxy groups exceeds 1.2 mass %; the amount of the gel fraction was 7.97 mass % at an epoxy group concentration of 1.4 mass %.

Compatibilisation of PP and a liquid-crystal copolyester Vectra A900 (LCC) following the reactions between the epoxy groups of poly(ethylene-*co*-GMA) (EGMA) containing 12% GMA with the hydroxy and/or carboxy groups has been studied.[45] It was found that the EGMA graft LCC is formed at the PP – LCC interface and the surface tension decreases. Blending was carried out in a co-rotating twin-screw extruder (d = 30 mm) in the temperature range 265 – 290 °C. The PP – LCC blends thus obtained possessed higher elongations at break and impact strengths. The LCC domains were found to be of smaller size and the crystallinity of the modified PP was lower than that of the blends prepared by conventional (mechanical) technique. The use of ethyltriphenylphosphonium bromide as a catalyst improves the blend compatibility owing to grafting.

A broad class of polymer blends based on polyamides (PA) was obtained.[1] Compatibilisation by the strengthening of the interaction between the blend components is a major way of modification of toughened materials.

Kudva *et al.*[46] studied blends of Nylon-6 with acrylonitrile/butadiene/styrene terpolymer (ABS) and poly(styrene-*co*-acrylonitrile) (SAN) using copolymers of GMA with methyl methacrylate (MMA) as compatibilisators. The GMA molecules contain epoxy groups which can react with the terminal groups of PA, while poly(methyl methacrylate) (PMMA) can be mixed with the SAN phase of ABS at any concentration of acrylonitrile. Blends were prepared in a Killion single-screw extruder (Germany) (d = 25.4 mm; l/d = 30) at 240 °C and a screw speed of 40 rev min^{-1} or in a Baker-Perkins co-rotating twin-screw extruder at 240 °C and a screw speed of 170 rev min^{-1}.

The dependence of the mass-average size of the SAN particles ($\bar{d}_w$) on the GMA concentration in poly(GMA-*co*-MMA) is shown in Fig. 8. The complex shape of the curve describing the variation of $\bar{d}_w$ is due to chemical reactions between the epoxy groups and the amino and carboxy terminal groups of Nylon-6 at the interface (Fig. 9). Owing to the nature of the PA, the interdomain space is filled with loop-like and bridging structures.

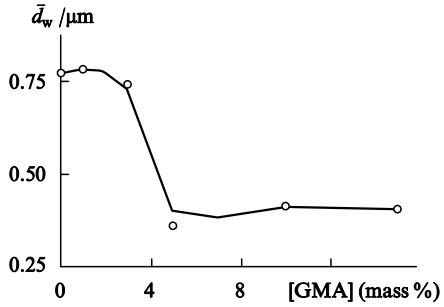


Figure 8. Dependence of the mass-average size of SAN particles on the GMA content in poly(GMA-*co*-MMA).
The blend ratio was Nylon-6 : SAN : poly(GMA-*co*-MMA) = 75 : 20 : 5. The SAN copolymer contained 25% of acrylonitrile. In the absence of poly(GMA-*co*-MMA), a blend with the ratio Nylon-6 : SAN = 75 : 25 was studied.[43]

It was found that the notched Izod impact strength decreases upon introduction of the copolymer containing 3 mass % of GMA (Fig. 10). When the GMA content was 5 mass % and 10 mass %, the impact strength increased. More intense mixing using a twin-screw extruder resulted in a substantial decrease in

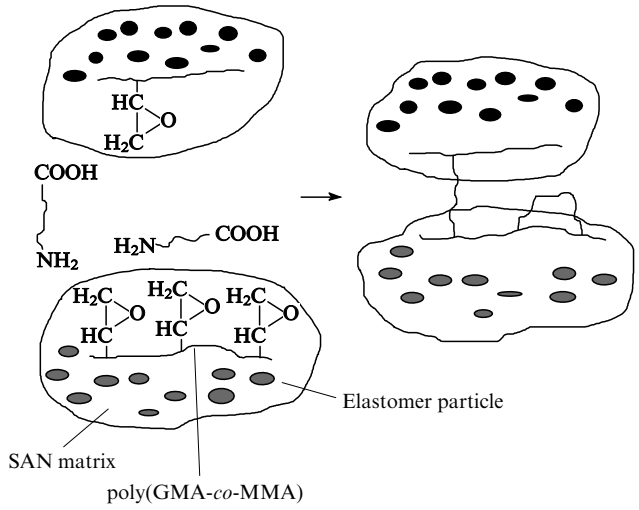


Figure 9. A scheme of the reaction between Nylon-6 and poly(GMA-*co*-MMA) in the Nylon-6 – ABS – poly(GMA-*co*-MMA) blend.[43]

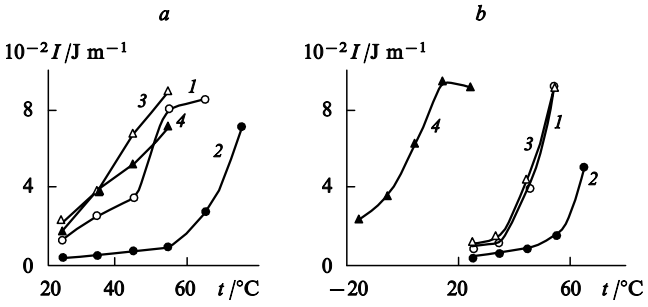


Figure 10. Temperature dependences of the notched Izod impact strength for Nylon-6 – ABS blend (*1*) and ternary blends Nylon-6 : ABS : (GMA – MMA) = 47.5 : 47.5 : 5.0 at a GMA content of 3% (*2*), 5% (*3*) and 10% (*4*) in single-screw (*a*) and twin-screw (*b*) extruders.[43]

the domains of the dispersed phase and in an increase in the impact strength.

V. Transesterification reactions and interchange processes

The kinetics of the transesterification reaction between poly(ethylene terephthalate) (PETP) and co[poly(PETP – *p*-hydroxybenzoate)] copolyesters (PHB – PETP) at blend ratios of 85 : 15, 70 : 30 and 50 : 50 in a Brabender Plasticorder mixer (Germany) at 275, 285 and 293 °C has been studied taking two types of the PHB – PETP copolyesters, with a PHB : PETP ratio of 40 : 60 (P46) and 60 : 40 (P64), as examples.[47] It was shown that the reaction is described by a second-order kinetic equation and the effective rate constant of the reaction depends on the blend ratio and temperature.

Yet another type of reaction, namely, interchange processes between a polyhydroxyether of bisphenol A and a segmented copolyetherester Hytrel, has been studied.[48] The copolyester is a thermoplastic elastomer comprising rigid crystallisable tetramethylene terephthalate blocks and flexible polytetramethylene – ether glycol – terephthalate blocks. Mixing of the components was carried out in a Brabender Plasticorder mixer. The kinetics of the interchange reactions was studied by tracing the torque variations. After mixing for 15 min, the interchange processes are completed to yield mainly branched and cross-linked products. The induction period was independent of the blend ratio and always exceeded 15 min at 240 °C.

Owing to specific interactions, the components of this blend are miscible at any ratios. Because of this, only one glass transition temperature is observed.

VI. Preparation of thermoplastic elastomers by dynamic vulcanisation

Among reactive blending processes in an extruder reactor, dynamic vulcanisation is the most promising for industrial use.[49] Thermoplastic elastomers (TPE), prepared from polymer blends by dynamic vulcanisation, are a specific class of materials which, on the one hand, can be processed in the molten state as thermoplastic polymers and, on the other hand, possess the properties of vulcanised elastomers at operating temperatures. Since they are quite competitive with conventional rubbers in the market, interest in these materials is currently increasing.[50]

The merit of TPE is their ability to be reprocessed. The properties of TPE do not change essentially upon reprocessing. This allows complete recycling and waste utilisation. Creation of polymer blends which can be non-waste processed is an important ecological problem due to the increasing accumulation of plastics waste and environmental protection demands.[51]

The history of the creation of different types of TPE up to the year 1987 has been considered in a comprehensive review by Legge.[52] Technological fundamentals of the preparation of modern types of TPE have been developed by Coran.[49] An *in situ* dynamic vulcanisation technique has been proposed, where vulcanisation of an elastomer proceeds simultaneously with its mixing with a thermoplastic polymer. This allows the preparation of blends with unique morphology characterised by 'dispersion' of the particles of the vulcanised elastomer in a continuous thermoplastic matrix. This technique permits the production of materials with excellent operating characteristics and these materials can be readily non-waste reprocessed.[53]

Polymeric compositions based on 11 different elastomers and 9 thermoplastic polymers have been considered.[49] Combining these elastomers and plastics allowed the preparation of more than 75 types of TPE.

1. The mechanism of dynamic vulcanisation

The properties of TPE depend on many parameters such as blend composition, the nature of vulcanising agents, blending conditions, temperature – time superposition during the formation of network structure of the elastomer, *etc.*

The preparation of TPE with improved mechanical properties requires mixing of dispersions of submicron sizes.[49, 50, 53] In particular, the tensile strength and elongation at break of the PP – EPDM-based blends (PP : EPDM = 40 : 60) increase with the decrease in the domain size (Fig. 11). In this case, mixing is superimposed on the cross-linking reaction which causes changes

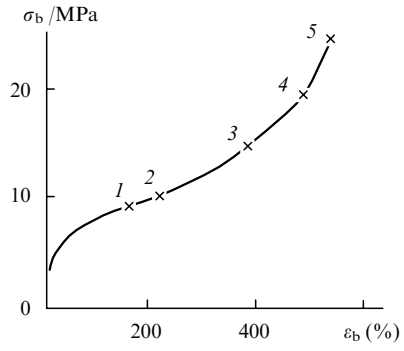


Figure 11. 'Stress – strain' diagrams for PP – EPDM blends (PP : EPDM = 40 : 60) with different domain size of the elastomer phase (× denotes a break).[49]
Number-average domain size /μm: (*1*) 72, (*2*) 39, (*3*) 17, (*4*) 5.4, (*5*) 1 – 1.5.

in the morphology of the elastomer phase, thus resulting in an increase in the viscosity of the medium and hampering the blend homogenisation. Therefore, efficient blending leading to a material with homogeneous submicroscopic distribution of the particles of the dispersed phase requires that the condition (1) be met.

The plots shown in Fig. 12 illustrate the effect of the density of cross-links, v_e, on the tensile strength σ_b and tension set ε_∞ of TPE. As can be seen, σ_b monotonically increases with increasing v_e, whereas ε decreases rapidly even at small v_e values. It is noteworthy that the rigidity of the material varies only slightly in this case.

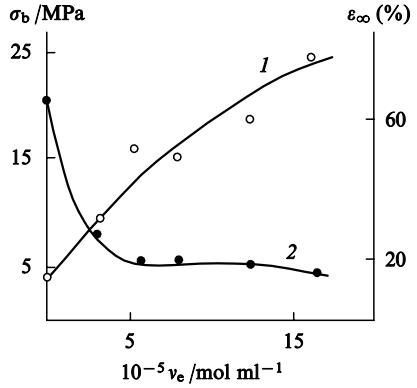


Figure 12. The effect of the density of cross-links v_e on the tensile strength σ_b (*1*) and tension set ε_∞ (*2*).[47]

Polypropylene-based TPE are usually prepared at temperatures above 180 °C. Degradation of TPE, which occurs at this temperature, detracts from the properties of the PP and elastomer phase.[54] If peroxides are used as vulcanising agents, degradation is accompanied by cross-linking. Therefore, the preparation of TPE with optimum properties requires knowledge of the parameters of temperature – time superposition during the formation of a network structure of the elastomer in the blend. Additionally, if the process is performed in the presence of peroxides, one should know the kinetics of (i) degradation and cross-linking of PP and (ii) the formation of interfacial polymer – elastomer links.

Regularities in the cross-linking and degradation of a polyisoprene elastomer SKI-3℠ at 190 °C have been reported.[55] The content of the sol fraction and its MMD was studied as function of the duration of vulcanisation at different concentrations of tetramethylthiuram disulfide (TMTD) and sulfenamide C (SA) used as vulcanising agents. Figure 13 presents typical gel chromatograms of the sol fractions of the SKI-3℠ elastomer cross-linked at different TMTD : SA ratios. After heating the main peak on the chromatogram of the elastomer is shifted towards the low MM region due to the depletion of the rubber fractions with the highest molecular masses. As can be seen, the rates of vulcanisation and degradation depend on the ratio of the components of the vulcanising system. For instance, for the same vulcanisation time of 3.5 min the system with the ratio TMTD : SA = 2 : 0 exhibits a bimodal distribution (Fig. 13 *a*), the system with the ratio TMTD : SA = 1 : 1 exhibits a shoulder (Fig. 13 *b*) while the system with the ratio TMTD : SA = 0 : 2 exhibits a broad unimodal distribution, which also covers the region of the initial molecular masses (Fig. 13 *c*). The existence of the limiting MM value of the sol fraction of the cross-linked elastomer was established [55] and it was found that this value remains virtually the same at any ratio of the vulcanising agents in the system. A similar picture was also observed in the case of prolonged vulcanisation carried out for 14 min (see Fig. 13, curves *3*).

The kinetics and mechanism of degradation of an elastomer – polymer blend can be significantly different. It was shown [56] that the induction period for the oxidation of PP – EPDM blends at

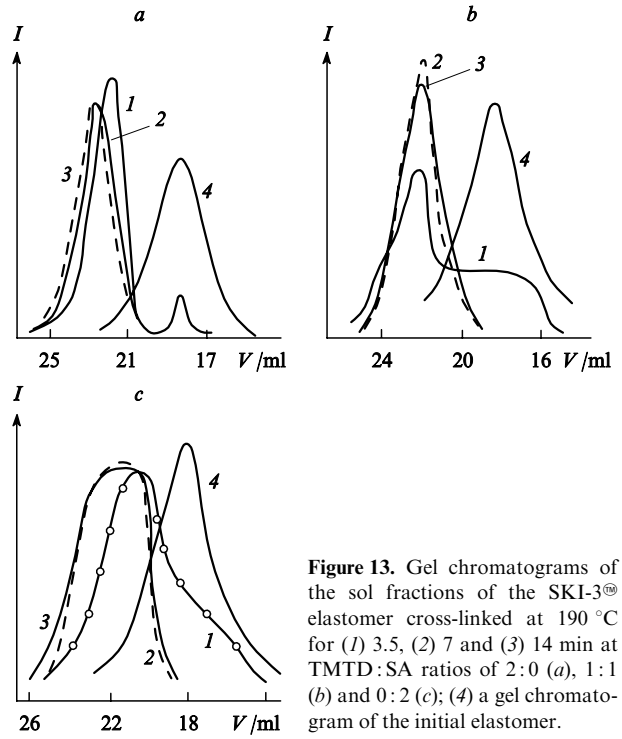


Figure 13. Gel chromatograms of the sol fractions of the SKI-3℠ elastomer cross-linked at 190 °C for (*1*) 3.5, (*2*) 7 and (*3*) 14 min at TMTD : SA ratios of 2 : 0 (*a*), 1 : 1 (*b*) and 0 : 2 (*c*); (*4*) a gel chromatogram of the initial elastomer.

110 °C is longer than that for the oxidation of the initial PP and can even be longer than the induction period for the oxidation of EPDM at a particular blend ratio. Upon introduction of vulcanising agents the oxidation resistance of the material increases and depends on the type of the vulcanising system of the rubber. Degradation products changes the blend morphology, thus changing the properties of TPE. This effect was particularly pronounced in the case of dynamic vulcanisation of ternary PE – PP – EPDM blends in the presence of peroxide as the vulcanising agent.[57,58] It was found that the tensile strength σ_b and modulus of elasticity E decrease with increase in the peroxide concentration in the blends with high PP content, whereas in the blends with high EPDM content these parameters increase under the same conditions. George *et al.*[59] showed that the cross-linking reaction dominates over degradation in the PP – nitrile elastomer blend in the presence of dicumyl peroxide.

The effect of the chemical nature and concentration of the vulcanising system on the properties of an EPDM – HDPE blend was studied.[60] The vulcanising systems investigated exhibited different induction periods and rates of EPDM vulcanisation. The sulfur-containing vulcanising system exhibited the shortest induction period and the highest rate of vulcanisation, whereas the resin-based system exhibited the longest induction period and the lowest rate of vulcanisation.

Studies on the kinetics of vulcanisation of systems with different concentrations of vulcanising agents showed that the rates of vulcanisation remain virtually constant irrespective of the chemical nature of the vulcanising system as the concentrations of these agents is doubled or halved. On the other hand, the induction period lengthens as the concentration of the sulfur-based vulcanising system decreases and remains the same if the resin-based system is used.

It was shown [61] that the dependence of the density of cross-links in the ethylene/propylene/vinylnorbornene terpolymer on the peroxide concentration passes through an extremum.

Vulcanised EPDM samples exhibited the greatest tensile strength in the presence of the sulfur-containing system, while the largest elongation at break and tension set were attained if the resin-based system was used as the vulcanising agent. The tensile strength increased to some extent with increasing concentration of activators (the sulfur-containing system). A decrease in the con-

centration of the vulcanising agents caused some deterioration of the stress–strain properties and an increase in the elongation at break and tension set. Mechanical properties of the vulcanisates remained virtually unchanged in the presence of the resin-based system.

For TPE samples, the concentration of vulcanising agents had almost no effect on the rebound elasticity and hardness. The strain–strength properties of TPE improved with the increase in the concentration of the sulfur-containing system and deteriorated as the concentration of the resin-based system increased. A decrease in the concentration of the vulcanising agents caused a decrease in the tensile strength, while the elongation at break and tension set at break increased.

The effect of the chemical nature of the vulcanising system on the physical properties of the TPE based on the EPDM–PP blends can be followed from the data listed in Table 3.[62] As can be seen, TPE prepared with the use of the phenolic system exhibit better characteristics (especially, swelling in oil and tension set at compression).

Table 3. The effect of the chemical nature of the vulcanising system on the properties of TPE based on SKEPT℗–PP blends [EPDM : PP = 60 : 40 (mass %)].[62]

Property	Vulcanising agent		
	sulfur-containing system	dimethylol-alkylphenol	peroxide
D (arbitrary units)	43	44	39
σ_b /MPA	24.3	25.6	15.9
$\sigma_{\varepsilon = 100\%}$ /MPa	8.00	9.72	8.07
ε_b (%)	530	350	450
H (%)	194	109	225
ε'_∞ (%)	43	24	32

Note. The following notations are used: D is the Shore hardness; $\sigma_{\varepsilon = 100\%}$ is the stress at 100% elongation; H is the swelling in oil and ε'_∞ is the tension set upon compression (22 h, 100 °C).

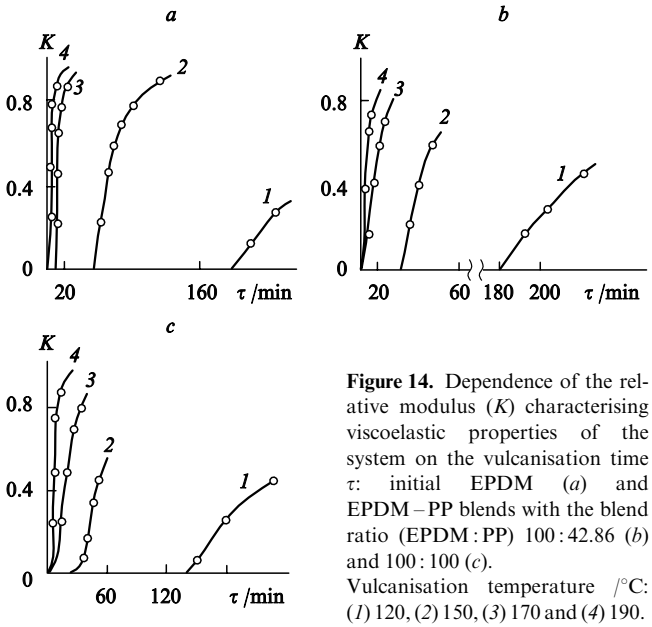


Figure 14. Dependence of the relative modulus (K) characterising viscoelastic properties of the system on the vulcanisation time τ: initial EPDM (*a*) and EPDM–PP blends with the blend ratio (EPDM : PP) 100 : 42.86 (*b*) and 100 : 100 (*c*).
Vulcanisation temperature /°C: (*1*) 120, (*2*) 150, (*3*) 170 and (*4*) 190.

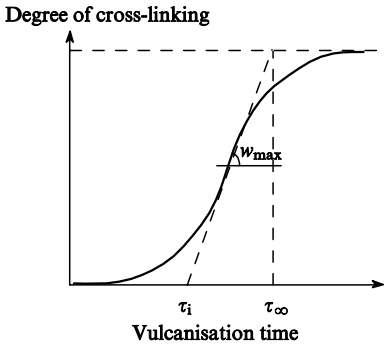


Figure 15. A schematic representation of the vulcanisation curve.

Does the thermoplastic polymer affect the kinetics of vulcanisation of the elastomer? Sengupta and Konar[63] studied this problem taking the vulcanisation of EPDM–PP blends in the presence of a sulfur-containing vulcanisation accelerator in the temperature range from 120 to 190 °C as an example. The blend ratio was varied from EPDM : PP = 100 : 0 to EPDM : PP = 100 : 100. Analysis of the vulcanisation curves revealed three time intervals corresponding to the main stages of vulcanisation (Fig. 14), *viz*., the induction period of the vulcanisation, the network formation period and the reversion period, respectively. The effective activation energy of vulcanisation varies only slightly, being equal to 8.85 kcal mol^{-1} for the initial elastomer and lying between 7.11 and 11.17 kcal mol^{-1} for the EPDM–PP blends. On the other hand, the induction period and the rate constant of the vulcanisation change.

Figure 15 presents a general pattern of a vulcanisation curve. In the second stage of vulcanisation, the degree of cross-linking, q, can be to a first approximation written as the following linear relation:[64]

$$q = w_{max}(\tau - \tau_i), \tag{4}$$

where w_{max} is the maximum vulcanising rate, τ is the vulcanising time and τ_i is the induction period. Preparation of a material with homogeneous submicroscopic distribution of the particles of the dispersed phase requires that the following condition [see the inequality (1) above] be met

$$\tau_m < \tau_i . \tag{5}$$

The time taken to reach the limiting degree of cross-linking (τ_∞) can be determined from the relation (4)

$$\tau_\infty = \tau_i + \frac{q_\infty}{w_{max}}, \tag{6}$$

where q_∞ is the limiting degree of cross-linking.

As to degradation, it has no pronounced effect on the material structure if

$$\tau_f < \tau_d , \tag{7}$$

where τ_d is the induction period of degradation.

The limiting degree of cross-linking should be reached during the time τ_f, therefore

$$\tau_\infty \ll \tau_f . \tag{8}$$

Based on the inequalities (5)–(8), a criterion for the choice of optimum temperature–time superposition during dynamic vulcanisation can be written as follows:

$$\tau_m \leqslant \tau_i \leqslant \tau_\infty \ll \tau_f < \tau_d . \tag{9}$$

The vulcanising agents and temperature-time superposition during the formation of TPE are chosen taking into account relations (9) and the criteria (10a)–(10c)

$$\tau_i \geqslant \frac{R^2}{6D}, \tag{10a}$$

$$w_{max} \geqslant \frac{1}{l/V - \tau_i} \quad (10b)$$

or

$$w_{max} \geqslant \frac{1}{\tau_d - \tau_i}, \quad (10c)$$

where R is the radius of the extruder and D is the effective diffusion coefficient.[64] These conditions hold if the vulcanising agents are introduced into the initial elastomer prior to blending.

The problem of the order in which the blend components are fed into the extruder reactor is also topical. For instance, by varying the order of the introduction of carbon black in TPE one can change the resistivity of the end product from 3.7×10^{13} to 2.5 Ω cm.

The knowledge of the order in which the components are fed into the extruder reactor and employment of the criteria (10a)–(10c) allowed the development of one-step dynamic vulcanisation.[65]

2. Structure and properties of thermoplastic elastomers

Thermoplastic elastomers represent two-phase systems in which cross-linked elastomer particles of size ~1 to 2 μm are uniformly distributed in the polymer matrix.[49, 50, 53]

Dynamic vulcanisation has been carried out in either a Brabender mixer or a Berstorff twin-screw extruder.[65] The temperature-time superposition as well as the type and order of feeding the blend components into the extruder were chosen with account taken of the criteria for the formation of TPE [relationships (10a)–(10c)]. Table 4 lists the results of mechanical and rheological tests of the TPE obtained upon varying the blend ratio. As can be seen, the rigidity and tension set of the TPE increase with the increase in the PP content, *i.e.*, the elastomeric properties of the TPE diminish. On the other hand, the rheological properties of the TPE are improved (the MFI increases). As the oil content increases, the rheological characteristics are also improved, while the strength characteristics deteriorate. Similar results have also been reported by Coran.[49]

Table 4. Effect of the TPE composition on their mechanical and rheological properties.

TPE composition			E_0 /MPa	E_{100} /MPa	σ_b /MPa	ε_b (%)	MFI[a]	D	ε_∞ (%)
[PP] (vol.%)	[EPDM] (vol.%)	M							
40	60	100	67	4.5	5.7	270	20.2	86	20
35	65	100	55	3.8	5.9	345	17.5	80	15
30	70	100	42	3.6	6.2	380	11.1	69	7
25	75	100	36	3.4	7.8	452	2.3	65	5
30	70	20	58	4.4	12.8	685	0.8	80	16
30	70	30	52	4.2	9.7	500	4.3	72	9
30	70	40	47	3.9	8.2	446	6.2	69	7

Note. The following notations are used: M is the oil content (in mass parts per 100 mass parts of the elastomer), E_0 is the initial modulus of elasticity, E_{100} is the modulus of elasticity at 100% elongation, D is the Shore hardness (in arbitrary units) and ε_∞ is the tension set.
[a] In g/10 min.

3. Deformation of thermoplastic elastomers

Deformation mechanisms of TPE have been poorly studied as yet.[66] It is unclear so far why the mechanical properties of TPE at room temperature are determined by the properties of the dispersed phase rather than of the matrix.[67, 68]

Figure 16 presents the stress–tensile strain diagrams of TPE in the coordinates $\sigma-\varepsilon$ at a tensile strain rate of 2.4×10^{-4} s^{-1} and different temperatures.[66] Similar patterns of the stress–tensile strain diagrams were also observed for other tensile strain rates. No 'neck' formation was observed in all cases. At $\varepsilon > 3\%$, the $\sigma-\varepsilon$ diagrams are well linearised in the coordinates $\sigma-(\lambda-\lambda^{-2})$, where $\lambda = 1 + \varepsilon$ (Fig. 16 *b*). At small elongations ($\varepsilon < 3\%$), a rapid increase in σ (a jump) was observed. The results obtained can be described by the following equation

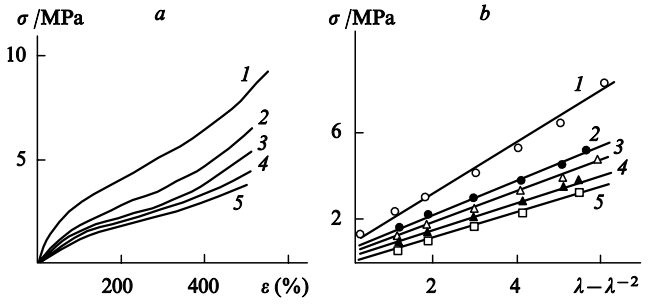


Figure 16. Stress–tensile strain diagrams $\sigma-\varepsilon$ (*a*) and $\sigma-(\lambda-\lambda^{-2})$ (*b*). The λ values at a tensile strain rate of 2.4×10^{-4} s^{-1} are given for 20 (*1*), 50 (*2*), 75 (*3*), 100 (*4*) and 125 °C (*5*).

$$\sigma = \sigma_0 + G(\lambda-\lambda^{-2}), \quad (11)$$

where σ_0 is the jump magnitude and G is the modulus determined from the slope of the straight line.

Thus, the overall stress is determined by the sum of two contributions, *viz.*, the stress which rapidly increases with the tensile strain and reaches the σ_0 value and the stress which linearly depends on $\lambda-\lambda^{-2}$. It was found that the jump magnitude, σ_0, decreases linearly with the increase in the temperature and is independent of the tensile strain rate (Fig. 17). At $T \to 145$ °C, $\sigma_0 \to 0$. This temperature corresponds to the onset of the melting of PP. Therefore, it was assumed that σ_0 is determined by the tensile strain of PP. The modulus G increases as the tensile strain rate increases and decreases with the increase in temperature.†

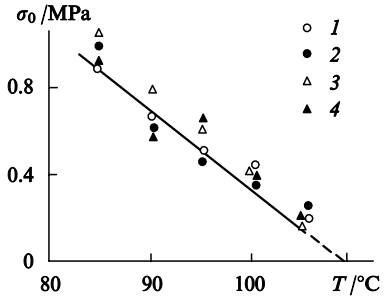


Figure 17. Temperature dependences of the σ_0 jump at tensile strain rates of 2.4×10^{-4} (*1*), 2.4×10^{-3} (*2*), 2.4×10^{-2} (*3*) and 9.5×10^{-2} s^{-1} (*4*).

The dependences of the tensile strength σ_b and elongation at break ε_b on the tensile strain rate $\dot{\varepsilon}$ and temperature are shown in Fig. 18. As can be seen, ε_b is temperature independent. As $\dot{\varepsilon}$ increases, the elongation at break decreases rapidly and then varies only slightly. The tensile strength, σ_b, is a linear function of $\log\dot{\varepsilon}$. The straight lines obtained for different temperatures are parallel to one another. The slope of the straight lines $\sigma_b - \log\dot{\varepsilon}$ is very small, which means that σ_b depends only slightly on the tensile strain rate.

Based on the results obtained, a structural model and a deformation mechanism were proposed for TPE.[66] At high PP

† Similar results for other types of TPE were recently obtained by S I Volfson, R R Grabdrashitov and K S Minsker *Russ. Polym. News* **5** (3) 1 (2000).

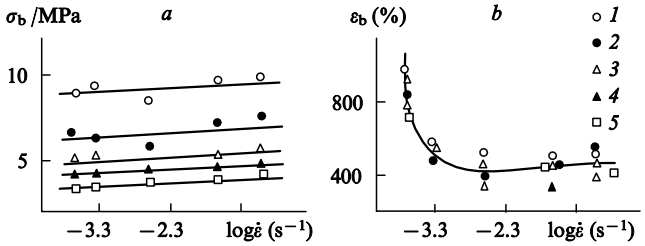


Figure 18. Dependences of the tensile strain (*a*) and elongation at break (*b*) on log$\dot{\varepsilon}$ at 20 (*1*), 50 (*2*), 75 (*3*), 100 (*4*) and 125 °C (*5*).

content in the blend, the cross-linked EPDM domains are linked by the PP chains; at high EPDM content, they are linked by the elastomer chains. The space between the EPDM domains and the links is filled with oil and PP spherolites (Fig. 19). Initially, only the PP matrix undergoes deformation, thus being responsible for the initial jump, σ_0. In further stages, deformation of the PP matrix occurs simultaneously with that of the dispersed EPDM phase.

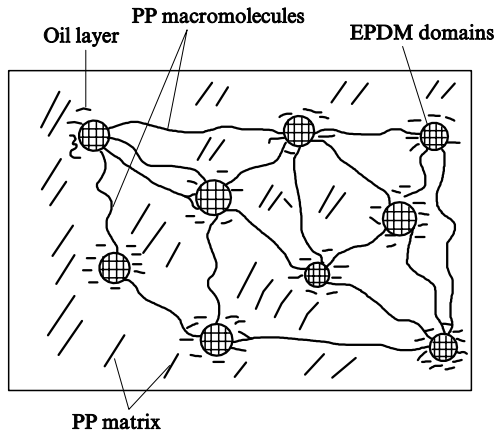


Figure 19. A scheme of the TPE structure.

4. Processing of thermoplastic elastomers

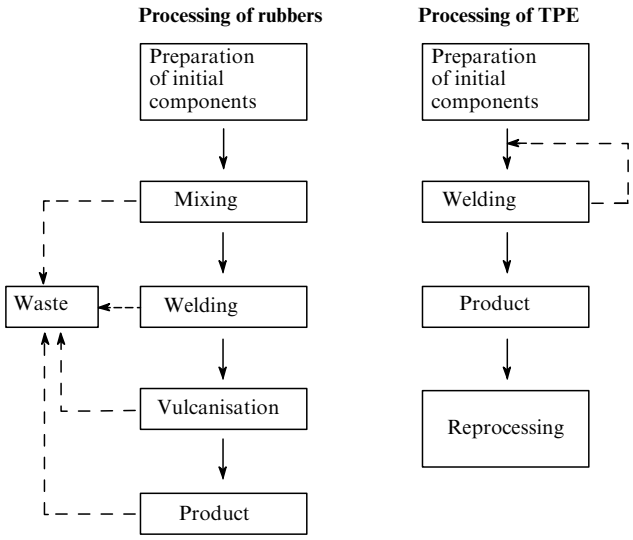
The processability of TPE depends on their rheological properties. Chung *et al.* showed [69] that in the molten state thermoplastic elastomers behave like the melts of filled polymers or rubber-modified plastics.

The properties of TPE allow their processing in the same manner as thermoplastic polymers, *i.e.*, by compression moulding, blow moulding, extrusion welding, calendering and thermoforming. Comparison of the production processes designed for rubbers and TPE (Scheme 1) reveals the major advantages of TPE, namely, easy processing, the possibility of re-moulding, multiple waste recycling, *etc*.

In the case of TPE, the process parameters are determined by the composition of the TPE and preparation conditions. The structure of the TPE specimens obtained by injection moulding has been studied [70] as a function of the radii of the specimens. It was found that the surface layers are highly oriented. A decrease in the process temperature leads to the formation of a disordered smectic structure in several TPE specimens and to a change in the EPDM : PP ratio in the layers owing to the orientation of the PP phase.

Yet another advantage of TPE as compared to the initial component (PP) is an increase in the highest operating temperature. It was shown [71] that at 280 °C the thermo-oxidative stabilities of the blends of PP with rubbers of different nature are higher and the mass losses are ~5 to 20 times smaller than those

Scheme 1



of the virgin PP (Fig. 20). Thermal stability of the polymer blends is independent of the blend ratio and is not determined by the thermal stability of the initial rubber (polyisoprene rubber SKI-3™, butadiene–nitrile rubber SKN-40™ or EPDM). It was also found that the thermal stability increases in the order PP–SKN-40™ < PP–SKI-3™ < PP–EPDM and is independent of the degree of vulcanisation of the elastomer.

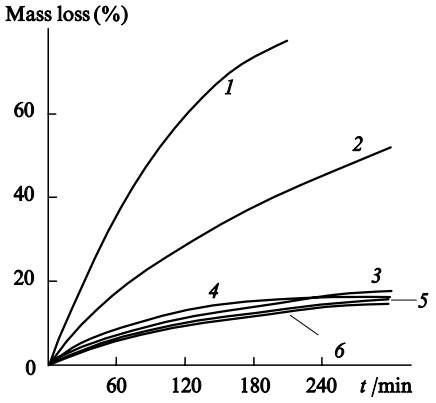


Figure 20. Isothermal TGA curves obtained at 280 °C in air for PP (*1*), EPDM (*4*) and PP–EPDM blends of compositions (PP : EPDM) (mass %) 95 : 5 (*2*), 20 : 80 (*3*), 50 : 50 (*5*) and 80 : 20 (*6*).

Replacement of traditionally used rubbers by TPE will make it possible to reduce the environmental pollution during their processing. These materials seem to be among the most promising materials to be used in the XXIst century and the areas of application of TPE are intensively expanded.

VII. Solid-phase reactions in an extruder reactor

Investigations into the solid-phase reactions in extruder reactors date back to the studies carried out by Academician N S Yenikolopyan at the N N Semenov Institute of Chemical Physics.[72] Solid-phase modification of polymers has an advantage over conventional modification techniques because it is more efficient and ecologically safe and permits substantial reduction of the cost of the end product.

1. Modification of polyalkenes

In studies on the solid-phase modification of isotactic PP and low-density polyethylene (LDPE) in the presence of maleic acid and its derivatives (maleic anhydride and sodium maleate) in an extruder reactor it was found that grafting depended only slightly on the presence of a radical initiator, *viz*., azoisobutyronitrile (AIBN).[73–77] The amount of the graft compound was found to be dependent on the intensity of mechanical treatment and the total mechanical energy supplied. The best result ($\sim$1.5 mass %) was obtained using the extruder reactor equipped with a set of cams which permitted the highest compression and shear stress of the materials. During processing, the particles of the PP phase undergo plastic deformation and breakdown.[78]

Mechanical properties of the solid-phase modified polyalkenes are much the same as those of the initial polymers. The modified polyalkenes exhibit adhesion to aluminium foil, which is more than an order of magnitude higher even at low degree of grafting (0.1 mass % to 0.2 mass %).[79,80] Degradation of the solid-phase modified polyalkenes is reduced as compared to the melt modified polyalkenes.

2. Modification of polysaccharides

The interest in natural polymers (in particular, polysaccharides) is due to the need for rational use of these materials and to the design of new ecologically safe processes. The most abundant natural polysaccharides are cellulose and chitin containing in the shells of crustacean and insects and in mushrooms.

Natural cellulose is widely used in the production of artificial fibres and films and in the textile industry.

Chitin and its deacetylated derivative, chitosan, are of considerable interest because they possess film-forming and fibre-forming properties and are biologically active compounds. Chitin and its derivatives are thought to be promising materials for biotechnological processes that use immobilised enzymes, for the creation of ion-exchange membranes for ultrafiltration and dialysis and for use as sorbents and ion-exchange resins. The complex-forming abilities of these polymers and their derivatives containing ionogenic groups can be used for selective extraction of metals from sea water.

Systematic studies on the solid-phase modification of natural polysaccharides under the joint action of high pressure and shear strain using different types of equipment[81] showed that under such conditions the polymers pass to the plastic flow state, which is accompanied by changes in their morphologies. This leads to a substantial enhancement of the reactivities of the polymers. These conditions have been employed to prepare three most abundant cellulose derivatives (alkali cellulose, carboxymethyl cellulose and cellulose acetate), chitosan (from chitin) and a number of its derivatives.

3. Modification of cellulose

The formation of alkali cellulose under the action of concentrated NaOH solutions on cellulose (mercerisation of cellulose) is one of the main stages of the process of viscose fibre production. Industrially, cellulose sheets are treated with a large excess of 18% aqueous NaOH (usually, the ratio of the volume of the liquid to the mass of cellulose varies from 20 to 40). This ratio is dictated by the necessity of complete and uniform swelling of cellulose. The large amount of waste water substantially detracts from the ecological characteristics of this process.

If mercerisation of cellulose is carried out in an extruder reactor, cellulose sheets are preliminarily milled and then the milled cellulose is treated with alkali solutions at a minimum volume of water. Depending on the initial concentration of alkali, the alkali cellulose thus formed differs in the degree of substitution of hydroxy groups, degree of polymerisation and some other characteristics.

Using the joint effect of shear strain and pressure on a mixture of cellulose with alkali allows the preparation of alkali cellulose with preset characteristics and improved properties, which is due to higher homogeneity of the product. Since in this case the amount of liquid is minimal, the process does not include the stage of removal of excess alkali solution. Here, water consumption reduces by an order of magnitude while alkali consumption reduces threefold as compared to the corresponding parameters of conventional procedures for the modification of cellulose. This to a great extent improves the ecological characteristics of the process.

Carboxymethyl cellulose (CMC) is one of numerous and valuable cellulose derivatives. Water-soluble CMC is widely used in the food, cosmetic and petroleum refining industry and in pharmacy.

Usually, CMC is obtained by treatment of cellulose with monochloroacetic acid (MCAA) in the presence of NaOH in an aqueous or aqueous-organic medium. However, this is accompanied by a side reaction (alkaline hydrolysis of MCAA) which nearly halves the efficiency of the procedure employed.

The ratio of the contributions of these reactions to the overall process can be changed by excluding water or any other dispersion medium from the reaction volume, *i.e*., by carrying out a solid-phase reaction under the conditions of shear strain.[82]

The yield of CMC increases with increase in the initial concentrations of MCAA and alkali in the blend. The degree of substitution varies in parallel and can be as high as 0.94. The efficiency of MCAA increases (up to 60% to 70%, *cf*. 50% for the conventional process); however, it decreases with increase in the MCAA concentration in the initial blend. Finely milled cellulose is much more reactive than coarsely milled cellulose and the CMC obtained from the former possesses a higher degree of substitution and solubility.

Cellulose acetates are used in the manufacture of artificial fibres, film, lacquers and plastics, so production quantities of cellulose acetates are rather large. Usually, acetylation of cellulose is carried out with acetic anhydride as the acetylating agent and with an acid (*e.g*., sulfuric acid) as the catalyst at 35–40 °C over a period of 4 to 6 h. It is known that cellulose acetates with a high degree of substitution cannot be obtained by treatment of cellulose with acetic acid. Strong intermolecular interaction in solid cellulose due to the formation of hydrogen bonds is the main factor precluding the esterification of the hydroxy groups of cellulose by acetic acid.

Figure 21 presents the dependences of the degree of substitution of hydroxy groups on the concentration of H_2SO_4 in the blend in the acetylation of cellulose by different acetylating agents under normal conditions and under the conditions of joint action of high pressure and shear strain. Acetylation by acetic acid under normal conditions results in the formation of cellulose acetates with a low

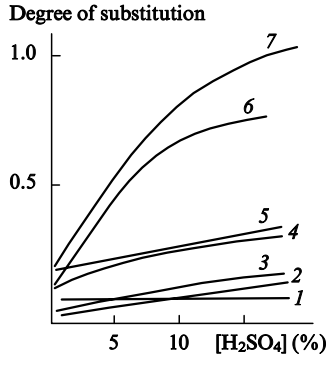


Figure 21. Effect of the concentration of H_2SO_4 on the degree of substitution of the hydroxy groups of cellulose in acetylation under normal conditions (the duration of the acetylation reaction was 4 h, at 20 °C) (*1–3*) and under plastic flow conditions (p = 1 GPa) (*4–7*).
(*1*, *5*) Cellulose : CH_3COOH = 1 : 3, (*2*, *7*) cellulose : CH_3COOH (glacial) = 1 : 3, (*3*, *6*) cellulose : $(CH_3CO)_2O$ = 1 : 1.5, (*4*) cellulose : : CH_3COOH (glacial) = 1 : 1.5.

degree of substitution. Treatment of cellulose with acetic anhydride yields cellulose acetates with higher degrees of substitution.[83]

If the process is performed under the conditions of plastic flow and high pressure, the degrees of substitution for all acetylating agents are higher than those observed under normal conditions.

4. Delignification of wood

Wood is a multicomponent polymeric system. The existing technologies for chemical processing of wood with the aim of cellulose production have some drawbacks. The loss of the wood content in the course of processing is nearly 50% and the amounts of toxic wastes and waste gases are large. Purification of these wastes presents severe difficulties. Modification of the technologies for wood processing to obtain wood pulp in such a way that the yield of the end product be 90% to 95% would allow substantial reduction of toxic waste and waste gases.[84]

A study on the model processes of delignification of wood and mercerisation of cellulose using Bridgman anvils has been reported.[85] The specimens were exposed to the joint action of high pressure and shear strain. It was found that under these conditions the above-mentioned processes proceed without an activation barrier. The activation energy for the delignification of wood by means of alkali cooking was found to be 32 kcal mol^{-1}.[86]

Delignification of wood in an extruder reactor resulted in products with fibrous structures. The reason is that the plastic flow of wood under the joint action of pressure and shear strain occurs mainly along the boundaries of strong, rigid fibres. This results in cleavage of the inter-fibre links and, correspondingly, in degradation of the wood. The fibrous products obtained in the extruder reactor exhibited improved mechanical properties as compared to those of the products prepared by conventional methods.

5. Preparation of chitosan and its derivatives

Chitin is less reactive than cellulose. This is due to specific features of its molecular and supramolecular structure, strong hydrogen bonding and a less active surface.

Chitosan is usually obtained by long-term treatment of chitin with concentrated NaOH solution at elevated temperatures. The existing technology for the production of chitosan is rather inefficient and requires high energy expenditures, the use of a large excess of aqueous alkali solutions and subsequent utilisation of alkali waste and waste water. It was shown [87] that the grinding of chitin and chitosan in a solvent in an extruder reactor leads to partial breakdown of the crystal structure. This appreciably enhances their reactivities towards etherification and leads to some decrease in MM.

Deacetylation of chitin in the temperature range 25 – 200 °C has been studied.[88] An increase in the excess of NaOH favours an increase in both the degree of deacetylation and solubility of the products obtained. The preparation of nearly completely deacetylated product with a solubility of 90% requires only a fivefold molar excess of NaOH, whereas conventional procedures for the preparation of chitosan require at least 10 moles of NaOH per 1 mole of chitin. Both the degree of deacetylation and solubility of the product can be increased by lengthening the residence time of the reaction system in the extruder reactor. Experimental studies showed that raising the temperature from 25 to 200 °C at the mole ratio chitosan : alkali = 1 : 5 results in an increase in the degree of deacetylation from 0.33 to 0.98 and in a substantial decrease in MM.

Conventional procedures for the preparation of chitin and chitosan carboxymethyl ethers are inconvenient since they are time-consuming, proceed as multistage reactions and require large consumption of reagents.[89]

A recently developed solid-phase method [90] for the preparation of these compounds allows improvement of ecological characteristics of the process owing to the absence of solvents and shortening of the reaction time from several hours to several minutes. The reaction was carried out in a Berstorff twin-screw extruder reactor. In the first stage, a mixture of chitin and solid NaOH was extruded at different ratios of the components. Alkali chitosan thus obtained was mixed with an alkylating agent (*e.g.*, MCAA dissolved in isopropyl alcohol or solid sodium monochloroacetate) and again fed into the extruder reactor (stage 2). The residence time in the extruder reactor was 3 to 5 min.

The effect of the reaction conditions on the properties of the reaction products can be followed from the data listed in Table 5. As can be seen, an increase in the concentration of MCAA and alkali leads to an increase in the degree of substitution, which reaches a maximum value of 1.4.

Table 5. Effect of the reaction conditions on the properties of the reaction products.

Specimen number	A	T_{react} /°C		P	$10^{-3} M$ (see note [a])	$x_1 + x_2$	z
		stage 1	stage 2				
1	1 : 4.25 : 2.0	absent	80	48	–	0.90	0.10
2	1 : 2.60 : 2.3	absent	80	20	47	0.40	0.62
3	1 : 4.80 : 2.3	180	120	30	5	0.51	0.32
4	1 : 5.25 : 2.5	100	100	70	82	0.70	0.35
5	1 : 5.25 : 2.5	200	100	68	6	0.68	0.29
6	1 : 8.40 : 2.9	120	120	65	70	1.02	0.25
7	1 : 8.40 : 4.0	80	60	70	90	1.40	0.20
8	1 : 2.60 : 2.3	100	100	46	62	0.65	0.45
9	1 : 4.40 : 4.0	100	100	58	45	0.87	0.27

Note. The following notations are used: A denotes the chitin : NaOH : MCAA mole ratio; P is the solubility in water (in mass %); x_1, x_2 and z are the degrees of substitution as regards the *O*-carboxymethyl, *N*-carboxymethyl and *N*-acetyl groups, respectively. Specimen 1 was obtained from chitosan and specimens 2 – 9 were obtained from chitin. Specimens 4 – 7 were obtained using a 40% solution of MCAA in isopropyl alcohol and specimens 8 and 9 were obtained using solid sodium monochloroacetate as the alkylating agent.

[a] The molecular mass of the soluble fraction of the end product.

The specimen prepared from chitosan in one extrusion step (see Table 5, specimen 1) exhibited a relatively high degree of carboxymethylation (0.9) at smaller consumption of MCAA. The molecular mass decreased dramatically as the temperature increased. This feature is common to solid-phase extrusion-modified polymers.

Solid-phase reactions of chitosan with a higher fatty acid (stearic acid) and with dicarboxylic acids (oxalic, malonic and succinic acids) in a twin-screw extruder have been studied.[82] The residence time of the reaction system in the extruder was 3 to 5 min.

Reaction products of chitosan with higher fatty acids combine the properties of polymeric substances (film-forming, fibre-forming, thickening properties, *etc.*) and surfactants. They can be of interest as amphiphilic materials for the preparation of solid and hydrogel membranes. Modification of chitosan by lipophilic compounds with the aim of enhancement of both the surfactant properties and the ability not only to thicken but also stabilise the food and cosmetic compositions containing oils and lipids is also topical.

The addition of stearic acid to chitosan proceeds mainly by an ionic mechanism. Reactions of chitosan with dicarboxylic acids occur as both the ionic and covalent linking. Studies on the reactions of chitosan with phthalic, succinic and maleic anhydrides showed [89] that these compounds react mainly with the amino groups of chitosan and that the degree of conversion increases with increase in temperature.

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