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GRAFT POLYMERISATION, POLYMER GRAFTING OF CELLULOSE AND CELLULOSE MATERIALS

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Principle of graft polymerisation

THE mutual interaction between cellulose and plastics has led in recent vears to more and more complicated and improved products capable of capturing an extensive share in the paper, board and packaging industry. In most finishing processes, whether they are concerned with the substance of the paper or its surface properties, the maintenance of the morphological structure of cellulose is of decisive importance. This is because the features associated with this structure, especially those of sheet formation and in contrast to synthetic finishing materials, have an enormous influence upon the combined technological properties of the finished product. Indeed, various cellulose derivatives and modified celluloses are known that would achieve the properties obtained when synthetics are added for finishing purposes, but they have the disadvantage in most cases that the fibre structure of cellulose is lost on modification. Therefore, it is not surprising that most composite paper and cellulose products, apart from a few products used mainly in the textile industry, represent an aggregate of the fibre and finishing material.

Whereas the bonding between cellulose and synthetic finishing material is achieved analogously to the fibre-to-fibre bonding of cellulose (mainly through hydrogen bonds of the added components), in graft polymers, a covalent bond is believed to exist between the cellulose backbone-molecule and the monomer side-chain. From a purely chemical point of view, one must differentiate among different mechanisms in the production of graft polymers of this kind, yet no explanation is given for the possible initiation, propagation and termination reactions-

- (graft polymerisation) 1. Cell+nM \rightarrow Cell-(M)_n
- 2. Cell+nM \rightarrow Cell+(M)_n
- 3. Cell+(M)_n \rightarrow Cell-(M)_n
- 4. Combinations of: (a) 1 and 2; (b) 1, 2 and 3; (c) 1 and 3 (under certain conditions)

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(Where *cell* represents a cellulose molecule and M represents the monomer used)

Reaction 3 can proceed, unwished for, along with reaction 1. Nevertheless, it is possible to bring about reaction 3 with finished polymer, this being known as polymer grafting (see later).

Suitable catalysts, capable of initiating and letting the reactions proceed with appropriate speed, are necessary for these reactions. One must differentiate among various initiation systems, which can be radical or ionic in nature.

Initiation

Radical initiators

CHEMICAL radicals used as initiators are mainly peroxides, peracids and peresters of organic and inorganic nature, which decompose thermally into radicals. Various azo-compounds also belong to this group of reactants—for example, 2,2'-azobisisobutyronitrile, which (by splitting at the nitrogen double bond) decomposes into two radicals according to the following mechanism—

Redox initiators

(a) In the presence of ferrous ions, hydrogen peroxide can decompose into hydroxyl radicals as follows—

$$Fe^{2+}+H_2O_2 \longrightarrow Fe^{3+}+OH^++OH^-$$

(b) It is known that alcohols react with cerric salts to form radicals. This is shown in the following equation—

Cell H+Ce⁴⁺
$$\rightarrow$$
 Cell · +H⁺+Ce³⁺

This method of initiation was extensively used when grafting cellulose and cellulose derivatives. In nearly all cases, grafted products without homopolymers originated. One drawback of this process is its long reaction time, thereby making it uneconomical.⁽¹⁻⁴⁾

Radiation initiation

As well as the radical activators described above, whose decomposition into radicals represents a function of temperature, other methods serving as a basis for a radical reaction mechanism are known. In these, high energy radiation (ultra-violet, electron, gamma-rays or X-rays) is effectively the catalyst. A number of researchers have often used high-energy radiation. Cotton was used as a backbone molecule, a method specially used for grafting textiles. J. C. Arthur and co-workers used as a radiation source 60 Co and grafted several vinyl compounds on cellulose. $^{(5-6)}$ In this context, vapour phase grafting of cotton is to be mentioned.

Through the addition of various organic sensitisers such as anthraquinone, anthraquinone derivatives and various vat dyestuffs, graft polymerisation can be initiated even by radiation in the visible region. The main condition here is that in their electronic spectra these sensitisers show a so-called $n \rightarrow \pi^*$ transition in the region of their longest wavelength absorption.^(8, 9)

Other initiators

In this section are included cationic and anionic initiators, which frequently find use in various special polymerisation processes. Catalysts that favour a carbonium ion mechanism are to be found among various halides and acids (for example, BF₃, BCl₃, BBr₃, AlCl₃, SnCl₄, TiCl₄ or H₂SO₄, H₃PO₄). Iodine, sulphur dioxide, silver chlorate, triphenyl methylchloride and others also belong to this group. On the other hand, alkali metals or alkali organic compounds favour a carbanion mechanism.

Inclusion

To DETERMINE the optimum conditions, the first experiments were carried out with 'inclusion cellulose'—that is, the cellulose was swollen in water or in an alkaline solution, following which the aqueous swelling medium was replaced successively by organic solvents. The preliminary treatment conditions have a significant effect upon the final graft polymerisation yield.

The primary swelling of the cellulose in water or alkali is of special importance, in that the hydrogen bonds of the cellulose micelle structure are loosened or broken; this leads to an increase of the specific surface, simultaneously with an extension of the network system and an increased readiness to react, especially the primary hydroxyl groups. Associated with this is an increased accessibility.

Robertson,⁽¹⁰⁾ Broughton & Wang⁽¹¹⁾ have shown that, when cellulose is swollen in various media, the strength of the fibre bonding is reduced because of a loosening of the hydrogen bonds. This results in a reduction in tensile strength, which depends on the polarity of the 'included' medium. A highly polar medium aids breakdown of the intermicellar hydrogen bonds, thereby enhancing reactivity by increased accessibility. Infra-red measurements on cellulose treated with deuterium oxide (D_2O) ,⁽¹²⁾ as well as diamagnetic measurements on alkali-cellulose⁽¹³⁾ confirm this view.

By investigating the 'inclusion' time and media, we have been able to

determine their fundamental effect upon the yield and speed. Because it is a two-phase or three-phase mixture, this effect can be strengthened or weakened by the diffusion speed of the monomer or the activator towards the macromolecule.



Fig. 1—Dependency of the peroxide retention of cellulose on inclusion time and peroxide retention as a function of the concentration of available peroxide

Dispersion medium	Dipole moment	Tensile strength, kN/m		
Water	1.84	0.09		
Methyl alcohol	1.65	0.45		
Diethyl ether	1.15	1.02		
Acetone	2.85	1.12		
Toluene	0.40	1.18		
Benzol	0.00	1.14		
Carbon tetrachloride	0.00	1.33		

TABLE 1—DEPENDENCY OF THE BREAKING LOAD OF AN INCLUSION PAPER ON THE DIPOLE MOMENT OF THE INCLUSION MEDIUM

Analogous data are available for the production of acetylcellulose (viscose), etc. The grafting reaction of cellulose with vinyl monomers, observed by

Krässig & Schrott⁽¹⁴⁾ for the acetylation of cellulose follows largely the dependency of the degree of modification on the degree of cellulose inclusion and on the dipole moment of the inclusion medium.

Further proof of this is the observed lattice plane extension of cellulose alcoholates, represented as a function of the ion radius of the alkali or alkaline earth ions.⁽¹⁵⁾



Fig. 4—Dependency of the graft yield on the ratio of the mixture BMA-methylmethacrylate (MMA)



Fig. 6—Lattice plane separations for several cellulose alcoholates represented as a function of the ionic radius of the cations present





In the course of this development programme, grafting experiments were performed with high energy radiation: X-rays as well as beta and gamma radiation.

The following results are from an experiment with a ¹³⁷Cs source with an activity of 180 000 Ci.⁽¹⁶⁾ The samples, together with monomer, were enclosed in ampoules, placed under the source and subjected to a definite dose of radiation. The yield and quality of the graft polymer were extremely variable depending upon the monomer used, so that the reproducibility of these experiments could not be guaranteed and economical utilisation was out of the question.

Technology of the new process

JUST as with the experiments described in the literature for the graft polymerisation of cellulose and cellulose derivatives, the techniques described here require a time-consuming pretreatment of the paper in the form of 'inclusion' in various swelling media. Relatively long reaction times do not play an important role for products, which of necessity require a lengthy and time-consuming pretreatment (as for the modification of wood), but paper finishing processes are usually performed at high machine speeds.

In addition, a few processes use expensive metal catalysts such as manganese (Mn^{3+}) initiators.⁽¹⁷⁾ These have a somewhat negative influence upon the physical properties of the end products. A further disadvantage, technologically as well as economically, is the requirement for an inert atmosphere that is, an oxygen-free nitrogen atmosphere. The most remarkable feature of all these processes is the very long reaction time, which varies from a few minutes to 100 hours; a decisively prohibiting factor for their economical exploitation.⁽¹⁸⁾ Furthermore, the graft products were interspersed with a large percentage of homopolymer, which had to be removed by a lengthy extraction process. The aim of further work therefore was to eliminate these disadvantages as described above.

On the other hand, the newly developed process (now to be discussed) differs from those known up to now in several respects. No kind of pretreatment or cleaning of the cellulose or its derivatives (referred to after this as cellulose) was necessary to obtain grafting.

Vinyl monomers suitable for grafting (for example, vinylacetate or methylmethacrylate) can be grafted using this process without solvent, without emulsifier or without special dispersion agents for the cellulose. At the same time, in so far as they are liquid under normal conditions, they serve as a dispersion medium for the radical catalysts necessary for the grafting reaction —for example, peroxides or 2,2'-azobisisobutyronitrile—as well as crosslinking agents with two or three functional groups available for polymerisation, as they are generally known in polymer chemistry.

Furthermore, instead of using the pure monomer or a monomeric system or a monomer solution, one can start in certain cases with a solution of the corresponding polymer. This situation was represented at the beginning of this paper in equation (3). This method, the so-called 'polymer grafting' as distinct from pure graft polymerisation, has to a certain extent the advantage of giving polymers or copolymers with defined physical and chemical properties.

The grafting can be carried out in two different ways-

Continuously (a) with the help of a heatable calender or (b) the impregnated or sprayed cellulose web may be grafted further in a heated drying tunnel (for example, with infra-red heating or in an airfloat dryer).

Discontinuously in a plain press.

Which of these processes is to be preferred depends upon the final product required. Variables of the process are temperature, pressure and machine speed. It is surprising and convenient that the reaction time fits the process very well.

Pure cellulose, cotton, sulphite and sulphate pulps, groundwood, filled papers, surface-modified papers, regenerated cellulose ester and ether, as well as related polysaccharides (such as starch and wood) are suitable for grafting.

The graft yield depends upon the morphological structure of the macromolecule and partly upon the concentration of the added filler. Increasing the porosity of the paper leads to an increase in the yield with non-extractable polymers under otherwise constant conditions.

Starting materials for the reactions are represented by the general formula-



(where R_1 , R_2 , R_3 , R_4 represent a hydrogen atom or a functional group)

A short impregnation or a spraying of the cellulose with the respective monomer (including additives) is sufficient to initiate the grafting—that is, the frequently long inclusion times previously necessary for the formation of different inclusion celluloses capable of reacting are no longer required. The soaking or spraying time is controlled in the continous process by the machine speed. The choice of monomers is determined by the desired physical, chemical and technological properties of the products desired from the grafting.

Peroxides, peracids of inorganic and organic nature, as well as azobisisobutyronitrile, with various additives are suitable as initiators for the grafting. Initiators together with additives are dissolved in the monomer or in the monomer mixture or in a solution of the oligomer.



Fig. 8—Dependency of the graft yield on the radiation dosage of a ¹³⁷Cs source, monomer vinylacetate (VAc)



Fig. 9-As for Fig. 7 and 8, monomer styrene



Fig. 10—As for Fig.7–9, monomer vinylpyrrolidone



Fig. 11—The graft yield plotted as a function of the reaction time in a plain press at different pressures



Fig. 12—Dependency of the breaking load on the reaction temperature of various chemical pulps



Fig. 13—Dependency of the graft yield on the reaction temperature for various monomers (acrylic ethylester, VAc, vinyl-proprionate, BMA)

The reaction may be regulated within wide limits by control of pressure, temperature, initiator concentration and reaction time. If pressure, initiator concentration and reaction time are held constant, the temperature may be used as a control variable to obtain maximum yield.

It is obvious that the properties of the grafted product depend not only upon the experimental conditions during the production process, but also decisively upon the monomers used. For example, monomers that possess hydrophilic functional groups (such as methacrylic acid) will yield products with hydrophilic absorptive and ion-exchange properties.

Using this method and depending upon the choice of monomer, an improvement can be obtained in the breaking load, wet strength, tearing and bursting strengths, hydrophobic nature and, to some extent, the absorptivity; air permeability, water vapour permeability, grease resistance, dimensional stability and ion-exchange ability can also be improved. Furthermore, a few of the products may show bacteriostatic and flameproof properties. Additionally, the products, after such treatment, may be weldable and heat-sealable and exhibit, depending upon the pressure region in which the grafting was carried out, opaque or transparent properties.

The products may show paper, film, foil or textile-like characteristics, depending upon the base materials. Consequently, a large number of applications are possible for special papers such as for packaging, printing, chromatography or hospital bed linen.

Several practical applications are concerned with the grafting of beechwood veneer to reduce or even eliminate the uptake of water. Much experience has been gained with the calender and airfloat drying methods. This latter method allows a combination of graft polymerisation and polymer grafting. This is clearly demonstrated by Tables 2 & 3, which show results for a cigarette tipping paper and for a calender roll paper having considerably improved thermal stability.

(ILOAT DRIER METHOD)									
Property	Raw paper MD CD		V_1 , 10 m/min MD CD		V_2 , 20 m/min MD CD				
Suction head, cm Duration, 10 min	1.45	1.15	0.93	0.85	1.15	0.95			
Breaking load, N 12 h curing	30.0	11.3	32.4	11.3	32.1	30.9			
Wet tearing strength, N 30 s dip in distilled water	—		4.7	1.66	3.42	0.88			

 TABLE 2—RESULTS OF THE GRAFTING OF CIGARETTE TIPPING PAPER (FLOAT DRYER METHOD)

B 3—TESTS ON THE IMPROVEMENT OF THE THERMAL STABILITY OF CALENDER ROLL PAPER WITH ACRYLONITRILE (FLOAT DRYER METHODS) <i>Estimation of the breaking load, N</i> Graft	ıt		Graft	aft erised	CD	19.6	
	treatmen	treatmen 220°C		polym	MD	33-3	
		Thermal	17 h at		aper	CD	13·2
				Raw p	DM	16.2	
		190°	Graft Raw paper polymerised	polymerised	CD	45	
	Thermal treatment 24 h at 190°				ПD	89	
		$2\frac{1}{2}h$ at		aper	CD	42	
				Raw I	MD	76-5	
	aft erised, nout rature ment			CD	31.4		
	Gra Grander (Grander) Grander (with	temper treatr		MD	67	
	aper in	aper in ress, eated		CD	44		
	Raw po the p dry tr		ШD	83			
		paper			CD	42	
TABL		Raw	Raw		ΠD	80	



Fig. 14—Wet strength of grafted papers as a function of the reaction time, monomers VAc, acrylic ethylester, vinylproprionate, BMA



monomer VAc



Fig. 16—Percentage increase in the breaking load of grafted papers as a function of the reaction temperature, monomer VAc



Fig. 17—Percentage increase in burst as a function of reaction temperature, monomer VAc



Fig. 18—Dependency of the yield on the reaction temperature plain press method (VAc)



Fig. 19—Graft yield as a function of machine speed (calender method)



Fig. 20—Photomicrograph of ungrafted filter paper $\times 2000$



Fig. 21—Photomicrograph of a filter paper grafted with VAc in the steam phase (yield 100 per cent) $\times 2000$



Fig. 22—Photomicrograph of a radiation grafting of paper; monomer styrene (yield 95 per cent) $\times 2000$



Fig. 23—Photomicrograph of grafted paper, press method; monomer VAc (yield 8.4 per cent) × 2 000



Fig. 24—Photomicrograph of paper grafted with VAc, press method (yield 15.5 per cent) $\times 2000$

Further work has been carried out with capacitor tissue papers. Here, the monomers used have to be precleaned very thoroughly, otherwise the quality of the product suffers. Finally, a few photomicrographs of grafted papers made by using different grafting processes are shown in Fig. 20–24.

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Transcription of Discussion

Discussion

Dr K. Ebeling I would like to draw attention to two points—stress relaxation and change of modulus. I used dry paper in my study of moisture content (determined by Karl Fischer titration below 0.25 per cent). I did not observe the Kubát behaviour; there was no clear break point when plotting the relaxation speed against the unrelaxed load. The behaviour that I observed was similar to that in your Fig. 9 for the 4 per cent curve.

The other point is that the apparent initial straining modulus decreased after cycling that involved apparent plastic deformation. Only during cycling with relatively high average load did one observe that the slope of the load elongation curve was higher than the initial slope starting from zero load.

Mr A. A. Robertson We clearly have differences between us to resolve. We, too, have carried out these tests under completely dry conditions (at least as dry as anhydrous calcium sulphate can provide) and obtained the Kubát curves for a wide variety of papers. We have been able to relate the local modulus (which we measure after stress relaxation) to a local cycling modulus that also has been determined. We have found the local cycling modulus anywhere along the stress/strain curve to be higher than the initial modulus and very close numerically to that measured after stress relaxation. So our results are in direct contrast to your own.

Dr A. de Ruvo I think that Dr Robertson touched upon very important matters—what is the mechanical effectiveness of the latex in the paper structure and how do different ways of polymer deposition in the paper influence the mechanical effectiveness of the polymer? In our studies, we have worked with a torsional pendulum to measure the amount of polymer that is effective by following the damping curve with temperature. At the glass temperature, the polymer displays a damping peak, which is proportional to the amount of polymer present and mechanically active in the system. Of course, there are different ways in which the polymer can be deposited in the paper. One way is that it is between the fibres, where it constitutes the fibre bond; this is the

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most effective way if you want to use the polymer properties. The other way is on a free segment, where it is not taking any mechanical action at all; this is a very poor way of using the polymer. For Fig. G, where we have plotted the area of damping against the amount of binder, we used two different ways of putting the polymer into the system—spray bonding and beater addition. The curve shows that spray bonding is much more effective as indicated by the much higher increase in the area of the damping peak at specific loading levels.



The same situation is shown for a more practical property—strain. Spray bonding is again the effective process for putting the polymers into the sheet.

A small comment about the colloidal system. Of course, when you are using better deposition, you have to have a colloidal system and use a retention agent. In Fig. H, we have plotted binder retention against the percentage of the retention agent (Lufax, in this case). As expected, if we overdose the system, the binder retention falls. What is important is that, exactly at the point where the retention falls, the mechanical effectiveness (that is, the damping area) also falls. This means that the mechanical effectiveness of the latex is reduced by changes in the colloidal system. Besides this, of course, the reduction of retention means that an excess of latex exists in the papermachine system, which can be rather difficult.

Discussion

Mr L. M. Lyne With the increasing limitation of petroleum in the world, do you see a limitation in the development of polymer papers over the next 25 years?

Prof. B. G. Rånby No, I don't see that, because it is a very small fraction of the petroleum that goes into the preparation of polymers. It is at present only about 5 per cent, but the burning of petroleum is 85–90 per cent, so it is in this that restrictions in petroleum usage must first apply.