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Behaviour of Crosslinked Polymers

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Abstract

For application as components in an adhesive layer in photographic movie-films, five copolymers of methylmethacrylate and butylacrylate each with a different multifunctional comonomer, have been synthetized.

Depending on the copolymerizability of the multifunctional comonomers, adhesive layers with different mechanical properties were obtained. An approach towards an explanation for the diverging results from swelling and modulus measurements was worked out.

Introduction

In order to avoid undesirable reflections upon exposure to light, photographic movie-films may be coated on the backside with a removable black antihalation layer. This layer must be washed away before processing, in a separate prebad, followed by a rinsing bath.

When these photographic films have been cast on a polyethylene terephthalate support, an adhesive layer between the support and the antihalation layer is applied. The binding agent for this adhesive layer has to respond to three essential requirements.

In the first place it has to show sufficient cohesiveness in order to make the two layers adhere firmly to each other. In addition it has to be able to form a film layer, which is not removed by the alkaline prebath and the rinsing bath, in which the anti-halation layer is removed. Finally, after the removal of the antihalation layer, it should form a layer sufficiently resistant against abrasion and against common organic solvents (used in the photographic profession).

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In order to obtain such a binding agent, which satisfies these rather contradictory requirements (film forming and still sufficiently inert towards all kinds of solvent), the following concept for a copolymer synthesis has been put forward : a soft film forming acrylate polymer with residual incorporated double bonds, in an aqueous dispersion. Upon casting on the polyethylene terephthalate support these polymers are sufficiently film forming. Later on, possibly after a thermal post-treatment at 200°C (1), the residual double bonds can crosslink, resulting in a layer which is resistant towards abrasion and to solvent attack.

In this respect, a series of five acrylate copolymers, each having a different multifunctional comonomer (MFM) incorporated, have been synthetized.

On the basis of differences of physical chemical properties of the resulting films, these crosslinked copolymers can be classified, in the order of decreasing effect of the incorporated MFM on the mechanical properties. The first copolymers show the modifications of physical chemical properties that could be expected on the basis of Flory's theory, whereas the last three copolymers show deviating properties.

Experimental data

Five series of copolymers of methylmethacrylate (MMA) and butylacrylate (BA) with increasing amount of five different multifunctional comonomers (MFM) have been synthetized in the latex phase (see table 1).

TABLE 1

REF.	POLYMER COMPOSITION		CHARACTERISTICS	
	M.M.A. / B.A.	M.F.M. *	GRAIN DIAMETER nm	(η) 25° C T.H.F. **
NO CROSS-LINKING	50 / 50	.....	200	0.8
POL - 1	49.85 / 49.85 ↓ ↓ 46 46	0.3 ↓ E.D.M.A. 8	ca. 65 - 70	0.76 ↓ INSOLUBLE
POL - 2	IDEM	IDEM D.V.B.	ca. 40	0.76 ↓ 0.14
POL - 3	49.85 / 49.85 ↓ ↓ 46 46	0.3 ↓ T.A.O.E. 4	ca. 60	INSOLUBLE
POL. - 4	IDEM	IDEM P.E.T.E.A.	ca. 55	INSOLUBLE
POL - 5	IDEM	IDEM T.V.C.	ca. 35	INSOLUBLE

* E.D.M.A. : ETHYLENE DIMETHACRYLATE - D.V.B. : P. DIVINYLBENZENE - T.A.O.E. : TETRAALLYLOXYETHANE

P.E.T.E.A. : PENTAERYTHRITOL TETRAACRYLATE - T.V.C.H. : TRISVINYLCYCLOHEXANE

** T.H.F. : TETRAHYDROFURAN; ALL COPOLYMERS ARE INSOLUBLE IN TOLUENE

It can be deduced from measurements of the swelling factor (SF) of films made of these copolymers (see fig.1) that the SF for the five types of copolymers decreases accordingly to the amount of MFM incorporated into the copolymer. These results confirm that the MFM has effectively been incorporated and has given rise to crosslinking.

From these data and from the ratio proposed in Flory's theory between SF and modulus of elasticity $[G_t \simeq -5.3$ SF or $\log G_t \simeq -1.66 \log$ SF$]$, an analogous physical chemical behaviour for the five copolymers in film form could be expected. Although later findings (2), based on the kinetic theory of rubber, indicate that elastic moduli according to the equation $G_t = \frac{\rho RT}{Mc}$, give a better idea of the degree of crosslinking than SF measurements.

In our experiments it was found that only the copolymer with the first MFM shows the expected behaviour : rising Tg, and growing modulus of elasticity as a function of an increasing MFM content (see fig.2). Moreover the expected rise of the modulus of elasticity by a factor 10^3 appears at the temperature at which the Tg value is reached.

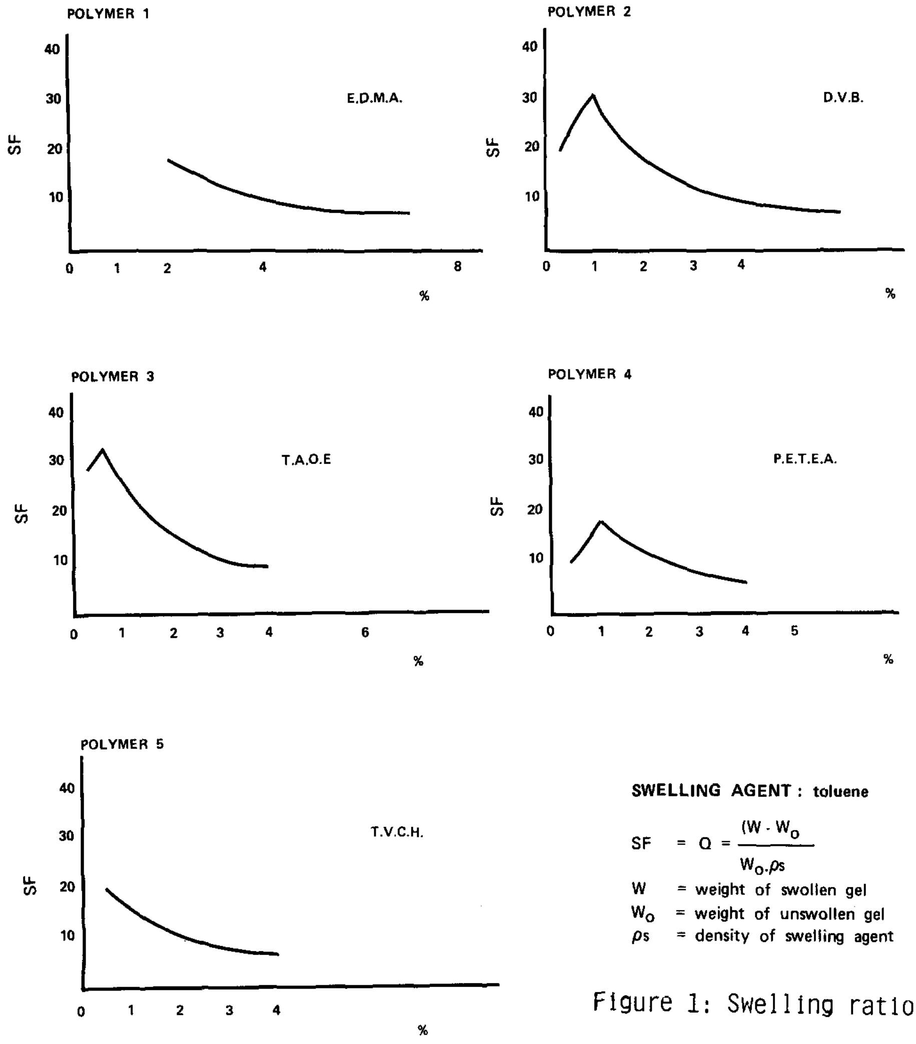
On the other hand, the copolymers with the other MFM's behave differently : smaller or no rise of Tg, and a much smaller modification of the modulus of elasticity (figs. 3, 4 and 5).

It should be noted that the mechanical properties of the films remain practically unchanged after the thermo-treatment, indicating that crosslinking has taken place during the synthesis or the film formation.

Discussion

In order to explain the observed phenomena, considerations along the following lines can be put forward. The films of polymer 1 (fig. 2) presumably consist chiefly of crosslinked copolymer chains, which have formed a homogeneous phase during the process of film formation. The higher Tg-value, the considerably increased moduli of elasticity below the respective Tg-values and the lower SF can thereby be explained (2).

The films of polymer 3 (fig.4) consist of a heterogeneous system of heavily crosslinked sequences,



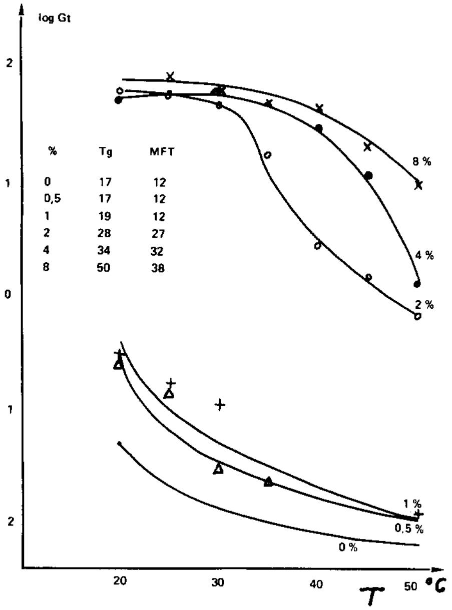
SWELLING AGENT : toluene

$$SF = Q = \frac{(W - W_o}{W_o . \rho s}$$

W = weight of swollen gel
W_o = weight of unswollen gel
ρs = density of swelling agent

Figure 1: Swelling ratios

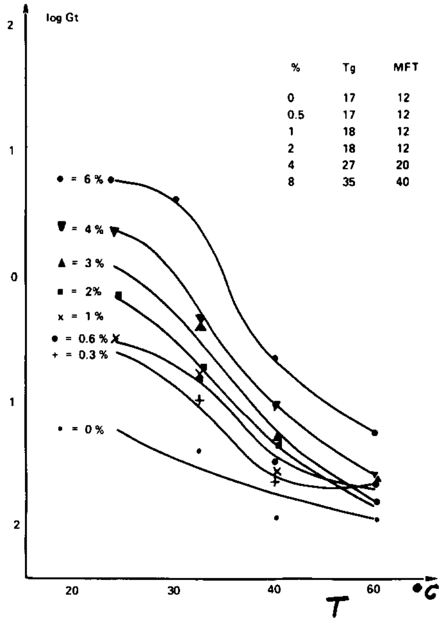
POL. 1 - E.D.M.A.



%	Tg	MFT
0	17	12
0,5	17	12
1	19	12
2	28	27
4	34	32
8	50	38

Figure 2

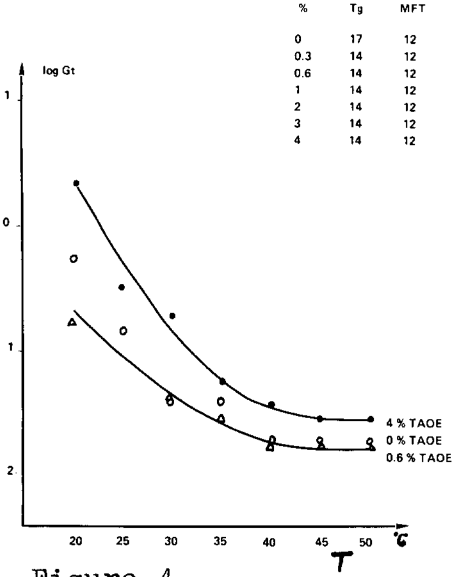
POL. 2 - D.V.B.



%	Tg	MFT
0	17	12
0.5	17	12
1	18	12
2	18	12
4	27	20
8	35	40

Figure 3

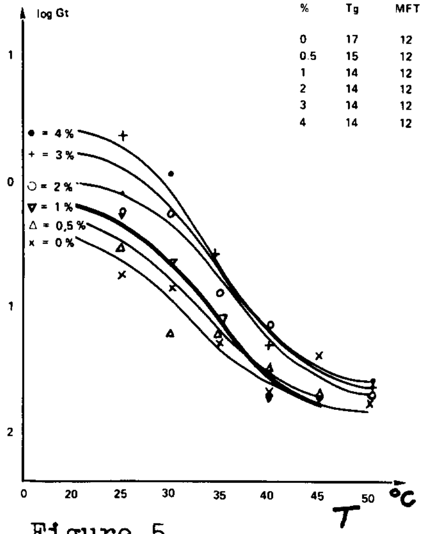
POL. 3 - T.A.O.E.



%	Tg	MFT
0	17	12
0.3	14	12
0.6	14	12
1	14	12
2	14	12
3	14	12
4	14	12

Figure 4

POL. 5 - T.V.C.H.



%	Tg	MFT
0	17	12
0.5	15	12
1	14	12
2	14	12
3	14	12
4	14	12

Figure 5

Moduli of elasticity as a function of the M.F.M. of various polymers.

within a matrix of long linear sequences. This "matrixé sequence is responsible for the film formation, and for the low Tg-values. It is also the modulus of this matrix phase, that can be derived from the stress-strain diagrams.

Both models would form the extremes of a series of intermediate possibilities. The behaviour of copolymers 2 and 5 (figs. 3 and 5) can be situated in this middle range of possibilities.

This diverging conduct is mainly governed by the copolymerization rate of the MFM's. For methylmethacrylate and ethylene dimethacrylate the copolymerizability is very favourable, resulting in a "statistical" incorporation of the MFM. For methylmethacrylate and p-divinylbenzene the copolymerization parameters also have similar values (r_1=0.6, r_2=1.3) so as to yield a system which is very close to that of polymer 1. For trivinylcyclohexane and (meth)acrylates, however, the copolymerizability is not adequate for obtaining a "statistical" incorporation of the MFM. In our laboratories the following r-values have been determined by means of the YBR (3) and Kelen-Tüdos methods (4), for the copolymerization of methylacrylate with trisvinylcyclohexane : r_1=2.7, r_2=0.01. These copolymers can be visualized as belonging to a different copolymer composition, based on very long sequences of linear chains, which can behave in a similar manner to that of non-crosslinked copolymers (2). For the allyl type MFM, finally, the poor copolymerizability with acrylate and other comonomers is well known and an even more extreme behaviour is logical.

Also the polymerizability of the pendant double bonds, which can crosslink, either during the emulsion polymerization (at a lower reaction speed) (5) or during the film forming or thermal post-treatment process, can have an influence on the properties of the copolymer films. As quantitative data are very scarce in the literature, further investigations in this direction may prove useful.

Conclusive remarks

The results of these experiments confirm the statement of Nielsen (2), who claims that mechanical tests, e.g. elasticity moduli, are more suitable and efficient for estimating the degree of crosslinking than swelling measurements.

Upon practical evaluation tests, it was confirmed that films manufactured with EDMA-monomer were most suitable for our purpose.

This research has been carried out in the frame of numerous fundamental research programs of many laboratories that is devoted to the study of the fundamental crosslinking reactions of addition polymers. It appears with more evidence than ever that this kind of investigation is very valuable not only for the photographic industry, but also for the whole multilayer technology.

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