

Fig. 1. The temperature dependence of the rate of the esterification reaction in EG, DGT, and OET for TPA of varied degrees of dispersion (S_{SP}, m²/g): 1) 0.1; 2) 0.5; 3) 1.5.

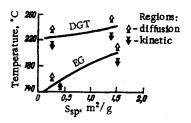


Fig. 2. The variation of the transition of the esterification reaction from the kinetic to the diffusion region with the reaction temperature and the specific surface of the TPA particles.

Thus, at a certain temperature the esterification of TPA of a given specific surface passes from the kinetic to the diffusion region and it is in the latter that the reaction rate is influenced by the degree of dispersion of the acid. The problem of the influence of the degree of dispersion on the macrokinetics of the esterification process is of considerable practical significance, more particularly because the process can be accelerated by using a TPA with an optimal degree of dispersion.

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THE "BLOCKING" AGENT OF THE ISOCYANATE

AS A FACTOR IN THE STRENGTH OF THE BOND

BETWEEN POLYESTER FIBRE AND RUBBER

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Isocyanates with shielded isocyanate groups are usually produced with phenol as the "blocking" agent [1, p. 128]. The use, however, of isocyanates "blocked" with phenol in the spinning preparation designed to improve the adhesion of polyester fibre to rubber [2], p. 303] is rendered difficult by the water insolubility of the block isocyanate and the toxicity of phenol.

In this article the influence is described of various blocking agents on the efficiency of adhesion compositions prepared from blocked diisocyanate and triglycidyl cyanurate (TGC). The influence of the mechanical factors was eliminated by carrying out the experiment with polyester monofilament 0.4 mm in diameter which was impregnated by immersion in water-acetone solutions of the adhesives, then dried for 15 min at 120°C, steeped in a standard latex-resorcin-formaldehyde composition, and finish-dried for 5 min at 180°C. The strength of the bond of the filament with rubber was tested with N blocks on rubber produced from a mixture of raw rubbers SKD-SKI.

A block-isocyanate with increased hydrophily can be produced by using polyethylene glycol as blocking agent. The writers produced 2,4-toluylene diisocyanate blocked with polyethylene glycol (TDIBPEG) with a molecular weight of 400 in the laboratory for the synthesis of textile auxiliaries of the All-Union Scientific

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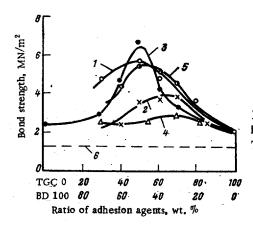


Fig. 1. The efficiency of adhesives containing TGC and blocked disocyanates (BD): 1) TDIBP; 2) HMIBC; 3) TDIBR; 4) TDIBPEG; 5) HMIBP; 6) untreated filament.

Research Institute of Synthetic Fibres. The original water-soluble product loses its water solubility after a heat treatment at 200°C in a mixture with TGC. It seems that an elevated temperature gives rise to the formation of a polyester urethan with a cellular structure as in the case of the composition of phenol-blocked 2,4-toluylene diisocyanate (TDIBP) with TGC [3, p. 67]. However, the strength of the bond of the filament with rubber was increased only marginally by an application of the composition TDIBPEG-TGC on the filament (Fig. 1). The strength of the bond in this case was on the level of that for a filament treated with TGC only.

An investigation by IR spectroscopy showed that, unlike TDIBP, TDIBPEG does not dissociate on heating to "open" isocyanate and PEG, a fact which is attributable to the lower activity of TDIBPEG as crosslinking agent for polyepoxide. The mechanical strength of a polymer with a low degree of crosslinking and containing long hydrophilic PEG chains is low so that the strength of the adhesive is also low. It follows that diurethan formed from PEG and 2,4-TDI cannot be used as component in an adhesive for polyester fibre.

The writers then used ϵ -caprolactam as blocking agent for isocyanate. Hexamethylene diisocyanate blocked with ϵ -caprolactam (HMDIBC) is regenerated on heating to isocyanate in the "open" form but in this case too the effect is considerably lower than for isocyanate blocked with phenol. It seems that phenol is an efficient crosslinking agent for TGC and therefore contributes significantly to the strength of the adhesive. The mechanism of the hardening of epoxy resin by phenol in the presence of diisocyanate can be illustrated as follows:

In these conditions ϵ -caprolactam will not harden the epoxy resin so that the adhesive composition HMDIBC-TGC is inefficient.

Thus, to increase the strength of the bond of polyester fibre with rubber the blocking agent for the isocyanate must be a substance which during the heat treatment of the fibre reacts with the ethoxy groups of the epoxy resin and thereby helps to give the hardening composition a branched structure.

In this context it was thought that biphenols like resorcin, hydroquinone, etc. may prove to be active blocking agents. Resorcin hardens TGC at an elevated temperature and is less toxic than phenol [4, p. 422]. The writers synthesized 2,4-TDI blocked with resorcin (TDIBR) by a method described elsewhere [5].

As in the case of TDIBP, the bond strength as a function of the components ratio in composition TDIBR-TGC contained a distinct peak. The maximum strength in this case was higher than that of composition TDIBP-TGC.

These experiments showed that the efficiency of adhesives for polyester fibre based on polyglycidyl ester and a blocked polyfunctional isocyanate depends to a significant extent on the type of blocking agent. The strength of the bond of polyester fibre with rubber can be increased by using a biphenol, e.g., resorcin, as blocking agent in place of the normally used phenol.

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FIBRE-FORMING AROMATIC POLYAZOAMIDES

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UDC [678,675:536,495].02:542,953

There is now a large body of experimental material on the synthesis of aromatic polyamides by low-temperature polycondensation in a solution and a number of conclusions have been reached in respect to the mechanism of this reaction [1-3].

The course of the reaction depends, however, on the nature of the monomer so that the mechanism of the polycondensation reaction must be analyzed in depth for every new polymer to be synthesized, the more so for the production of aromatic polyamides with azo groups the synthesis of which is not described in the literature. In this article the results are reported of an investigation of the influence of the ratio of the original monomers, the initial concentration of the monomers, and the temperature of the reaction on the logarithmic viscosity of polymers. The investigation was concerned with the reaction of dichloroanhydride of 4,4'-azobenzene dicarboxyclic acid (DCA ABDA) with a number of aromatic diamines.

The properties of the monomers and the method of synthesizing the polymers were described elsewhere [4]. The logarithmic viscosity of the polymers was determined for a solution of 0.5 g polymer in 100 ml amide solvent containing 3-5 wt. % LiCl at 20°C.

The diagram in Fig. 1 shows the influence of the ratio of 4,4'-diamino-2-phenylbenzimidazole to DCA ABDA for a varied batching time of the latter. The variation of the viscosity of the polymer with the batching time confirms Sokolov's findings [5] but differs slightly from them. The peak viscosity is reached after batch-

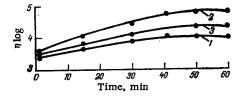


Fig. 1. The logarithmic viscosity of the polymer as a function of the batching time for DCA ABDA for various ratios of 4,4'-diamino-2-phenylbenz-imidazole to DCA ABDA: 1/1; 1/1.05; 1/1.1. Temperature 0°C; solvent DMAA + 5% LiCl.

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