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UV-polymerization of 2-ethylhexyl acrylate in interpenetrating polymer networks – some mechanical properties

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Summary

Interpenetrating polymer networks were prepared by photopolymerizing 2-ethylhexyl acrylate in the presence of polyurethanes derived from castor oil. The films obtained which contained varying amounts of both polyacrylate and crosslinking agent, hexamethylene diacrylate, were investigated as to their mechanical properties.

Introduction

An interpenetrating polymer network, IPN, is an intimate combination of two or more polymers in the form of networks, where at least one of them has been formed in the presence of the others. However, there is no chemical linkage between the distinct networks (1,2). Thus, IPN's can be prepared so as to exhibit some desirable properties by suitably choosing the polymeric components.

One point which arises when one deals with multicomponent systems is concerned with the degree of miscibility, which is related to the domain size of the microphases (3).

Experimental evidences show that miscibility among the components of an IPN increases gradually as the crosslink density of the networks also increases, so that the first network formed has a more pronounced effect (3,4). Thus, morphology can be controlled by regulating the crosslinking level of the networks. Changes in morphology can be followed through variations in physical and mechanical properties (2, 5-7).

In this work, IPN's from castor oil polyurethanes and poly(2-ethylhexyl acrylate), in different proportions, were prepared. The acrylate monomer was polymerized by UV irradiation in the presence of the polyurethane pre-polymer. Mechanical properties, as modulus, tensile strength and deformation at break, of films obtained were investigated.

Experimental

Polyurethane pre-polymers were prepared from castor oil (hydroxyl number 156 mg KOH/g) and toluene-2,4-diisocyanate (TDI) in appropriate amounts as to have NCO/OH molar ratios of 1.1, 1.6 and 2.1. The reactions were carried out at 60°C for 1 hr under a stream of dry nitrogen.

In the preparation of the IPN's, a mixture was added to each of the three pre-polymers, consisting of 2-ethylhexyl acrylate in different amounts, 10, 5 or 1% (in relation to the acrylate weight) of 1,6-hexanediol diacrylate (HDDA) and 5% (in relation to the acrylate) of benzophenone. The resulting mixtures were stirred for 15 minutes, cast onto glass plates and left in an oven at 55-60°C for 18 hr. The flms were irradiated for 36 hr and again stored in an oven for 4 hr at 120°C.

Tensile tests were performed on 5x70 mm strips, at least 5 specimens for each material, in

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an Instron 4202 equipment, at a cross-head speed of 50 mm/min, according to ASTM D 882-75b.

Results and discussion

Figure 1 shows modulus, tensile strength and deformation at break, as a function of NCO/OH for PU pre-polymers.

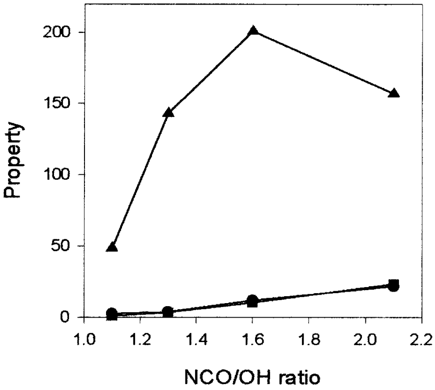
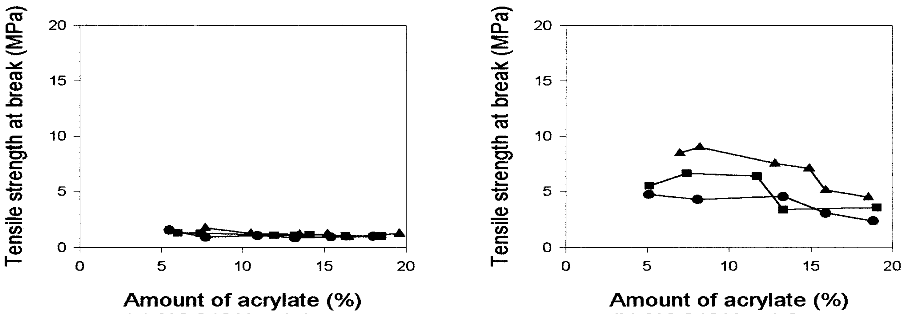


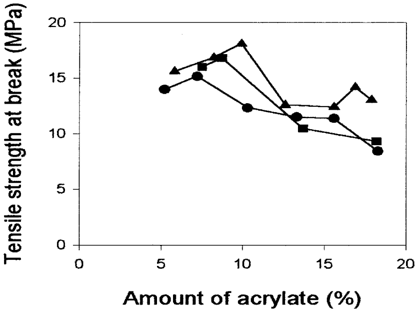
Figure 1: Mechanical properties of polyurethane pre-polymers with different NCO/OH ratios

Modulus as well as tensile strength increase gradually with NCO/OH due to increasing crosslink density due to allophanate linkages caused by the excess of TDI and gives rise to pre-polymer molecules having unreacted NCO groups.



(a) NCO/OH = 1.1

(b) NCO/OH = 1.6



(c) NCO/OH = 2.1

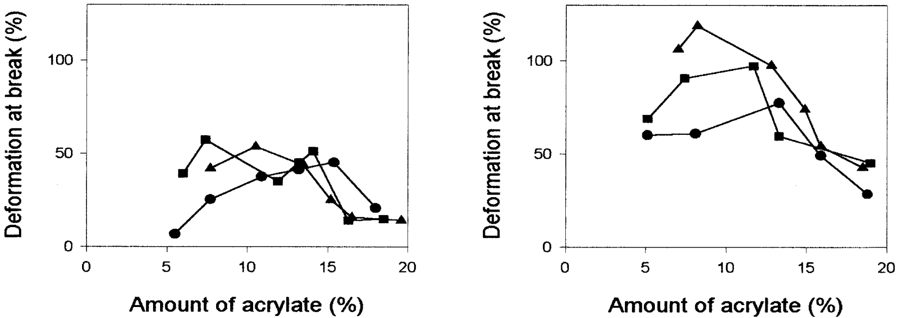
Figure 2: Tensile strength at break as a function of acrylate content

Differently, the deformation at break goes through a maximum which means that, after a certain value of NCO/OH, cumulative crosslinking makes the sliding of molecules passing one another more and more difficult. This can be credited to the formation of an increasing number of interconnections. The initial part of the curve would correspond to materials with enough reticulation to impart increased resistance to molecular sliding, without drastically affecting molecular mobility. This allows a progressive deformation up to a maximum. From this point on, related to a determined degree of crosslinking, chain mobility is severely influenced by the NCO/OH. With higher NCO/OH values, structurally more rigid polyurethanes can be formed, which would not permit large deformations.

From experimental observations it was found that polymerization of 2-ethylhexyl acrylate via UV-radiation is accelerated in the presence of the polyurethane. It was also observed that 2-ethylhexyl acrylate, in amounts higher than about 25%, promotes heterogeneous films characterized by corrugation and opacity, an indication that immiscibility develops. However, for convenience, all the materials prepared have been considered to be IPN’s.

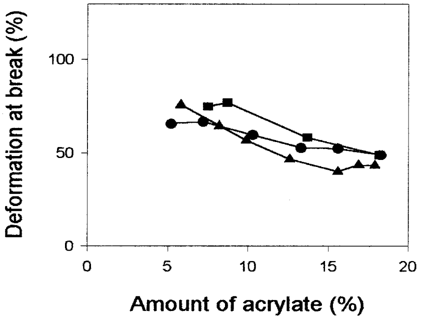
Figure 2 shows the variation in tensile strength as a function of the acrylate content in the IPN’s, for NCO/OH = 1.1, 1.6 and 2.1. As already mentioned in the literature (8-10), tensile data are not very sensitive to changes in the amount of acrylate.

Figure 3 shows deformation as a function of acrylate content for the three NCO/OH ratios used.



(a) NCO/OH = 1.1

(b) NCO/OH = 1.6



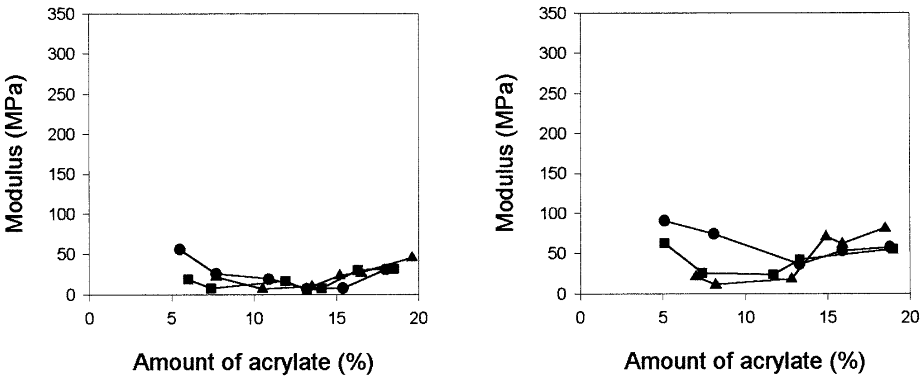
(c) NCO/OH = 2.1

Figure 3: Deformation at break as a function of the acrylate content

—●— 1% HDDA
—■— 5% HDDA
—▲— 10% HDDA

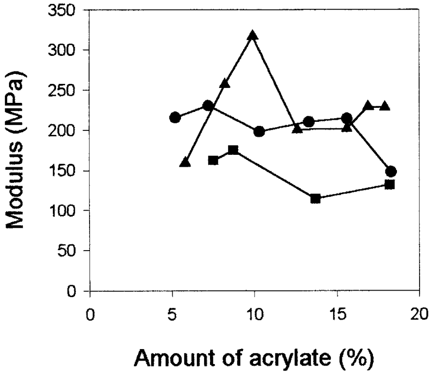
Comparing the curves in this Figure, an increase in the deformation is generally observed when NCO/OH goes from 1.1 to 1.6 and then decreases at NCO/OH = 2.1. Thus, IPN’s for which the pre-polymer has NCO/OH = 1.6 show better results for deformation than those with NCO/OH = 1.1 or 2.1. Considering now Figure 3b, 10% HDDA gave rise to larger deformations. In this case it can be thought that, despite the relatively high degree of reticulation in the acrylate phase, a polyurethane phase having an intermediate content of crosslinks can still retain flexibility, enough to withstand some deformation before failure. For NCO/OH = 2.1, the curves in Figure 3c show that as the amount of acrylate increases the deformation gradually decreases, pointing to a common value. Here, the addition effects of increasing the acrylate together with a high degree of crosslinking in the polyurethane phase do not leave much freedom for the network to deform.

Figure 4 shows how the modulus depends on the amount of acrylate. When NCO/OH = 1.1, Figure 4a, the influence of increasing amount of both acrylate concentration and crosslinking agent, HDDA, is small compared to IPN's with higher NCO/OH ratios.



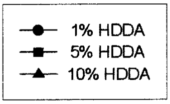
(a) NCO/OH = 1.1

(b) NCO/OH = 1.6



(c) NCO/OH = 2.1

Figure 4: Dependence of modulus on the acrylate content



However, as the NCO/OH is increased to 1.6 and to 2.1, Figures 4b and 4c, respectively, this influence becomes more significant. Nevertheless, a clear tendency is not observed since the curves cross each other, which suggests that sometimes the amount of HDDA and sometimes the acrylate concentration influences the modulus.

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