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The effect of gelation sequence on the mechanical properties of plasticized polyurethane-poly(glycidyl methacrylate) simultaneous interpenetrating network

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Summary

The simultaneous interpenetrating network samples with different gelation sequences based on plasticized polyurethane(PU) and poly(glycidyl mechacrylate)(PGMA) were prepared by changing the PU catalyst. The kinetics of network formation was monitored by FTIR. The obtained samples with different gelation sequences show opposite physical and mechanical properties. The sample with PU gelling first is transparent and brittle, while the sample with PGMA gelling first is opaque and highly elastic. The transmission electron microscopy(TEM) and dynamic mechanical analysis(DMA) methods were used to investigate the microstructures of these samples from different aspects to explain their completely different properties.

Introduction

The interpenetrating polymer network(IPN) technique, which seems to be the only way to bring thermoset polymers together, can often greatly improve the mechanical or other properties of polymers through its unique topological entanglement and interpenetration between networks. Simultaneous interpenetrating network(SIN) is easier to carry out compared to sequential IPN, the reaction process of which can be easily controlled so as to modify the properties of the final products, thus it was investigated more extensively. The research about polyurethane-polyacrylate SIN system has always been active. Many authors[1-6] have claimed enhanced mechanical or other properties for such materials, and found that the mechanical properties is non-montonic with the change of composition ratio between two components, and the maximum of mechanical properties appears at some point.

With respect to SIN, in the one-step process, also called *in situ* process[7], all components necessary to build up the final SIN are first mixed together, so the reaction speed of both network components can be manipulated to obtain different gelation sequence, which will definitely affect the microstructure and macrosopic mechanical properties of final products. The studies, however, concerning the effect of gelation sequence on mechanical properties are seldom reported, and most articles about gelation sequence concentrate on investigating the relation between gelation sequence and microscopic phase separation?[8-11]

In this article, the samples with different gelation sequences were prepared in our studied plasticized polyurethane-poly(glycidyl methacrylate) system by changing the catalyst of PU reaction. The apparently opposite physical and mechanical properties of the samples were found, which was thoroughly studied using TEM and DMA methods.

Experimental

Materials

Poly(ethylene oxide-tetrahydrofuran) (PET), with $\overline{Mn} = 3840$, donated by Liming research institute of chemical technology, was dried under vacuum. Modified hexamethylene diisocyanate(N-100), with functionality 3.62 was used as received from Liming research institute of technology. Triphenylbismuthine(TPB), obtained form Shanghai institute of organic chemistry, was dissolved in dichloromethane(DBP) to become a saturated solution when used. Glycidyl methacrylate(GMA), supplied by Luoyang Hengguang chemical corporation, was dried with molecular sieves before use. Dibutyltin dilaurate(T-12), dibutyl phthalate(DBP), and benzoyl peroxide(BPO) are produced by Beijing chemical plant. Dimethylamino benzaldhyde(DMAB) was produced by Sigma Co.

Preparation procedure

A one-shot method was adopted to prepare SIN samples. The required amount of N-100, PET([NCO]/[OH]=1.10) and GMA were mixed together with BPO(1.2 wt%), DMAB(0.72 wt%) and the plasticizer DBP(pl/po=1/1). The PU catalyst(T12 or TPB) was added last. The PU/PGMA ratio in all cases was the same(6/4 by mass). The mixture was cast into the teflon mold and put into the vacuum oven to degas, then was charged with nitrogen and elevated to 60°C curing for 4 days. For kinetic analysis, a drop of solution of the previous mixture was pasted between two NaCl plates mounted on the heating chamber.

Kinetics measurements

An FTIR spectrometer(Nicolet 560) was used for kinetic measurements, by averaging 16 scans, with a resolution of 4 cm^{-1}. Two NaCl plates(without gasket) were first heated to the desired temperature in a heating chamber supplement of the FTIR instrument before any measurements. Reaction conversion was calculated from the change of the normalized absorbance of the NCO peak at 2273 cm^{-1} and the C=C peak at 1637 cm^{-1}. The CH_2 stretching vibration at 2870 cm^{-1} was used as an internal standard.

Turbidity Measurement

Turbidity was measured with a 752C visible UV spectrophotometer. Turbidity τ was calculated through $\tau=-\ln(I/I_0)/L$, where I/I_0 is the transmittance of the sample with thickness L.

Tensile testing

The tensile strength and elongation were measured on an Instron-6022 tensile tester at room temperature(23°C) with a crosshead speed of 100 mm/min. Samples were cut to dumb-bell shape in accordance with ASTM 1708-95 standard.

Transmission Electron Microscopy

The electron micrographs were obtained with Hitachi H-800 electron microscope. The samples were frozen to -140°C and ultramicrotomed into 50 nm thick sections, which were Stained for 1 h in a 2% osmium tetroxide solution.

Dynamic Mechanical Measurements

The dynamic mechanical analysis was carried out on a Perkin-Elmer 7 Thermal Analysis system in the parallel plate mode. The temperature program was run from -100 to 100°C using a heating ramp of 5°C min^{-1} at a fixed frequency of 1 Hz. The testing samples were cut to column shape with *ca.* 3mm height and 5mm diameter.

Results and Discussion

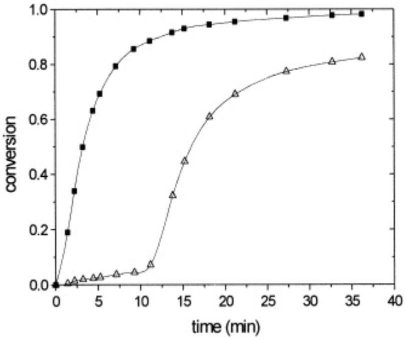


Figure 1 Conversion profiles of PU (■) and PGMA (△) at 60℃; PU catalyst: T-12 = 0.125%.

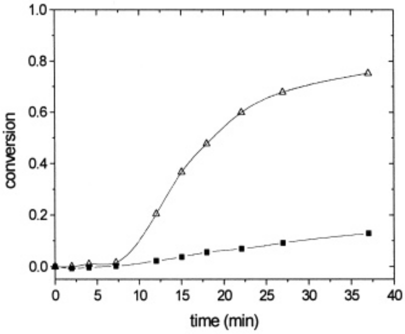


Figure 2 Conversion profiles of PU (■) and PGMA (△) at 60℃; PU catalyst: TPB = 0.02%.

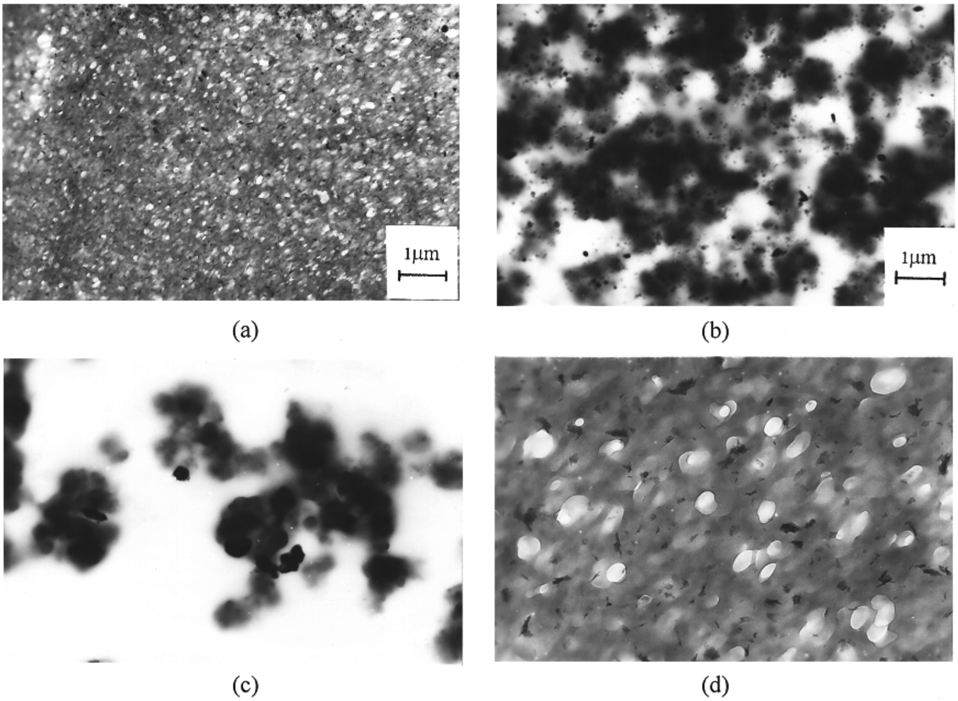
Two SIN samples with same formula but different PU catalysts were prepared in our laboratory. As shown in Figure 1 and 2, the kinetics of these two reactions was monitored using FTIR. When a large amount of catalyst T-12 was used, the PU reaction proceeded much faster compared with using the TPB catalyst, which is less active than T-12 in catalyzing PU reaction. Consequently, two different gelation sequences were achieved due to the different reaction speeds of PU components under the above two catalysts. The PU phase gelled first under T-12 catalyst(see Figure 1) since the PU monomer reached a high conversion in a short time (*ca.* 10 min), the PGMA reaction, however, nearly did not proceed at this time. The sample prepared under this condition was designated as SIN1, which represents PU gels first. On the contrary, the sample designated as SIN2 means PGMA gels first, in which the PU reaction proceeded slow using TPB as the catalyst.(Figure 2)

The physical properties of samples with different gelation sequences, i.e., SIN1 and SIN2, are quite different. SIN1 is a hard, brittle and transparent material, something like plastics; SIN2 is a soft, highly elastic and opaque material, just like rubber. Their mechanical and turbidity data and the data of pure PU are listed in Table 1 so as to compare with each other. It can be seen from the mechanical data that SIN2 presents fairly good mechanical properties, whose tensile strength and elongation are both greatly improved compared with the pure PU sample. However, the mechanical properties of SIN1 is very poor. This result really exceeds our expectations.

Sample	Tensile strength (MPa)	Elongation at break (%)	Turbidity
SIN-1 (PU gels first)	0.189	16.9	0.204
SIN-2 (PGMA gels first)	1.615	567.1	1.788
PU	0.591	95.0	0.172

Table 1 Effect of gelation sequence on mechanical properties of SIN

Turbidity can be used as an indication of the relative heterogeneity of the samples if the refractive index and volume fraction do not substantially change.[12] Usually, for a sample with thickness of 3-4mm, it is totally opaque when $\tau>1.0$ and becomes dim if $\tau>0.4$ and finally becomes completely transparent when $\tau<0.15$.[13] The turbidity data in Table 1 show that SIN1 and pure PU are both transparent, which indicates that SIN1 should be more homogeneous or have smaller phase domains compared with SIN2. It should be noted here that whether the sample is transparent or not is mainly dominated by the PGMA phase, since the pure PU sample is transparent but the pure PGMA sample is opaque.



(a) (b)

(c) (d)

Figure 3 TEM micrographs of SIN samples with different gelation sequence. (a) SIN1' (b) SIN2' (c) SIN2 (d) magnification graph of SIN1'

To find out the real situation of the microstructure, which may be helpful to understand the interesting mechanical behaviors, the samples were investigated through TEM.(Figure 3) To our regret, the SIN1 sample is too brittle to be ultramicrotomed, so two unplasticized SIN samples with the same recipe were prepared. These two samples with opposite gelation sequence have the similar physical properties as the plasticized ones, i.e., the sample where PU gels first(disignated as SIN1') is transparent, hard but tougher than SIN1; the sample where PGMA gels first(disignated as SIN2') is opaque, highly elastic and also tougher than SIN2. Accordingly, it is believed that the micrographs of SIN1' and SIN2' should reveal the same rule as the plasticized samples SIN1 and SIN2. The micrographs of samples with different gelation sequences are considerably different just as the macroscopic physical properties of the samples. The PGMA phase in SIN1' (white area in Figure 3 a) is dispersed phase, with small domain size, *ca.* 30~100nm (estimated from Figure 3 d). This size is smaller than visible light wavelength (400~700nm), hence the sample SIN1' is transparent. Contrary to this, in SIN2' and SIN2, the PGMA phase is continuous phase, the size of which is several to several hundred times larger than in SIN1' . This result agrees well with the fact that SIN2' and SIN2 are both opaque ones. Generally speaking, the phase formed first tends to form the continuous phase. The situation in micrographs just agree with it, i.e., the PU phase is continuous in SIN1' ; the PGMA phase is continuous in SIN2 and SIN2' . However, it is hard to explain the apparently opposite mechanical properties of SIN1 and SIN2 or SIN1' and SIN2' according to the results from TEM micrographs, because in SIN1' though the PU phase is continuous, the sample does not have the elasticity which should be possessed by continuous PU phase; in SIN2 and SIN2' though the PGMA phase is continuous, the samples present the highly elasticity which should not be possessed by the PGMA with plastic properties.

In order to explain the opposite mechanical properties caused by different gelation sequences, we investigated the samples from another approach, DMA, which can also reveal the microstructure of SIN materials just like TEM. The difference between DMA and TEM is that DMA reflects the interpenetration between networks on a molecular level, but the TEM presents the aggregation structure. As shown in Figure 4, the tanδ curves of SIN1 and SIN2 are obviously different. The SIN1 sample has two transition peaks corresponding to PU and PGMA transitions respectively. The SIN2 sample, however, has only one peak corresponding to PU phase, where the transition peak corresponding to the PGMA phase has disappeared and a new broad shoulder peak appears. The low temperature Tg transition of SIN2 shifts toward high temperature area compared with SIN1, which suggests a better interpenetration than SIN1. It follows that the molecular interpenetration in SIN1 sample is poor though it is transparent and possesses a smaller PGMA phase domain.

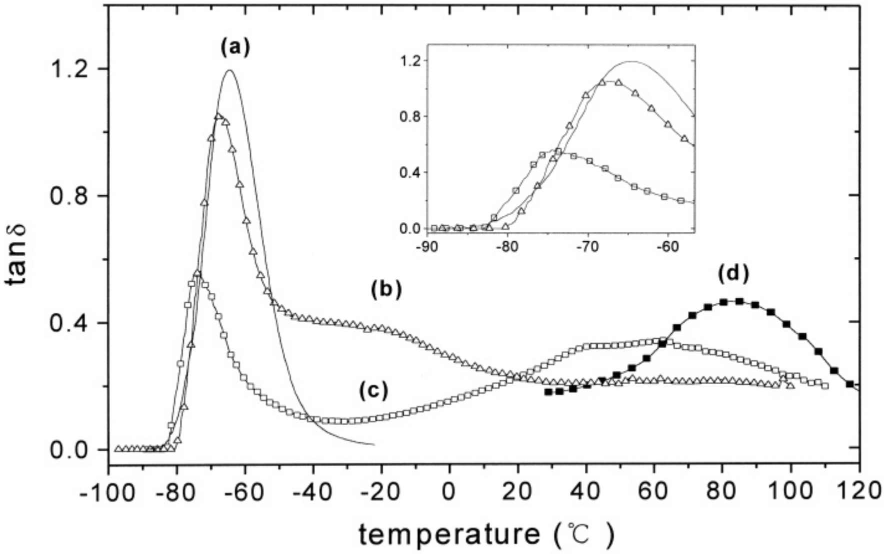


Figure 4 Tan δ vs. temperature plots for SINs and pure polymers. (a) pure PU*; (b) SIN2; (c) SIN1; (d) pure PGMA*. Insert: scale magnification of the low temperature region. *the plasticized ratio pl/po=1/1

It can also be seen from Figure 4 that the low temperature Tg transitions of SIN1 and SIN2 are lower than pure PU, which differs from the common case that the Tg transition peaks of SIN sample should shift inward compared with respective pure components.[2,4,6,14-17] This may be due to the effect of different plasticized ratio. Although the ratios of plasticizer to polymer, i.e., pl/po, are all 1/1 for all plasticized samples, as for the PU component alone, the pl/po is 1/0.6 in SIN samples, which is higher than that in pure PU sample. Consequently the Tg in SIN samples should be lower than in PU sample.

Summarizing all the above measurement results, we can thoroughly discuss the mechanical properties of the samples. In SIN1, where the PU monomers polymerize quickly and form the network first, the PGMA component still exists in the PU matrix in a form of GMA monomer when the PU component gels. The GMA monomer can grow rapidly to liner macromolecules according to free radical polymerization mechanism. As the PGMA macromolecules were formed, they were repelled by the PU network and could not interpenetrate with PU network well due to thermodynamic incompatibility. Finally the PGMA macromolecules accumulate together and disperse in PU matrix in a form of grannular filler, which seems to be the reason why SIN1 is the brittle material with poor mechanical properties. Although the interpenetration between two phases of SIN1 is poor(which could be proved from the two distinct tanδ peaks of DMA result), the "cages" formed by the first gelling PU network restrict the phase domain size of PGMA, which is smaller than the wavelength of visible light, thus the SIN1 sample is transparent.

In the case of SIN2(i.e. PGMA gelling first), PU network was formed according to step polymerization, and the molecular weight of PU increases gradually, therefore it is only when the PU reaction reaches some extent that the thermodynamic incompatibility between PU and PGMA phases will occur. However, due to the kinetic forced miscibility, i.e., PU has a network structure and it can interpenetrate into the preformed PGMA matrix but cannot be repelled out of PGMA, some PU molecular network can "stay" inside the PGMA phase and produces a PGMA/PU complex phase. The broad shoulder peak of SIN2 in Figure 4 most likely corresponds to this PGMA rich phase containing some PU molecules. Also the large white area in Figure 3c may indicate this complex phase. As a result the interpenetration shows a synergistic effect, that is, the tensile strength and elongation are all greatly improved.

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