

SEM COMPARISON OF TRADITIONAL AND MODULUS GRADIENT-INDUCED PARTICULATE COMPOSITES OF POLYURETHANE NANO POLYMER

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The microstructure of polyurethane (PU) nano material comprising hard-block urethane linkages and soft-segment prepolymer chains is presented and discussed. Two types of micro composites of the nano material are fabricated by reactive processing. A generic particle-doped composite is supplanted by the one in which a *modulus gradient* is deliberately introduced at the particle-matrix interface. SEM examines the morphology of the respective composites. Cryofracture surfaces of these composites reveal good interfacial adhesion in the modified composite without the attendant processing constraints and the visible particle pull out observed in traditional composites. The results are compared with parallel work comprising liquid crystalline polymer (LCT)-PET blend and a rubber-toughened epoxy. It is found that securing micro-particles to the host nano-matrix serves to increase the cohesive energy density, reduce the non-linear response and improve the fracture energy of the fabricated assembly.

Keywords: Polyurethane, Micro-phase segregation, Modulus gradient, Particle-matrix Interface, Reactive processing, SEM, Morphology

1. Introduction

Polyurethane (PU) is formed by the polyaddition reaction of hydroxyl containing prepolymer chains and diisocyanates [1]. Typical precursors and the corresponding segmented product are depicted in Fig.1. It is a multiphase material composed of hard and soft blocks as shown schematically in Fig.1. The OH differs in its backbone character. It could be polyether, polyester, or a polybutadiene structure. The type of isocyanate (-NCO) chosen depends on the degree of its reactivity.

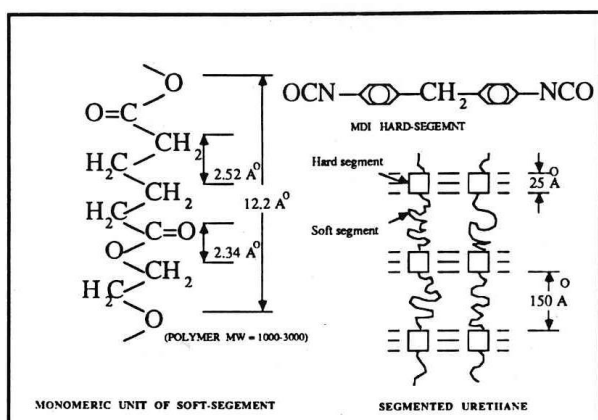


Figure 1. Precursors for a PU based on polyester prepolymer soft segment and MDI hard block.

The hard blocks in the PU mass are elastic, while the soft blocks are viscous in nature. The two

types of segments are segregated at the sub micron level. Together they provide a viscoelastic character to the material. Externally applied stress is partly recovered and partly converted into heat via viscous dissipation. The described behavior closely mimics the spring-dashpot system used as shock absorbers in automobiles. The spring provides the elastic recovery, while the viscous fluid in the dashpot absorbs and dissipates the shock into heat.

Polyurethane may be filled or foamed to give a wide variety of products ranging from automobile fenders to energetic composites to viscous dampeners. The latter field is the subject of a recent paper [2]. Hammer-milled glass-fiber reinforced polyurethane networks are finding increasing application in the automobile industry due to their light weight, high T_g , credible toughness and high modulus properties [3]. The addition of glass or mineral fibers can greatly reduce the linear thermal expansion of polyurethane, making it more compatible for steel mountings. Even in applications where linear expansion is not a problem, glass fibers help to improve dimensional stability and warpage.

Energetic polyurethane composites employ highly loaded solid crystalline particles. The mechanical properties of these systems are crucial to their dimensional and ballistic stability. Their ability to deform without rupture, and to recover is

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quite important for successful performance. If structural failure of the fabricated composite occurs by cracks in the matrix, fractures of the particle-matrix interface, or debonding under any applied load, it will lead to failure of the ballistic module in operation. It is, therefore, important to secure the system against such eventuality.

Although the polymeric matrix constitutes a small fraction of the micro-composite, it determines the principle mechanical properties. Thus, the cross-link density, the catalyst dosing, reactant equivalent weight ratio, and plasticizer content are conveniently varied to provide the desired mechanical properties. The strain capability is largely a function of the strength of the particle-matrix interface [4, 5]. During application of stress, a weak interface will cause separation of the particles from the matrix (dewetting), hurting the stress-bearing capacity to the detriment of mechanical properties, especially elongation.

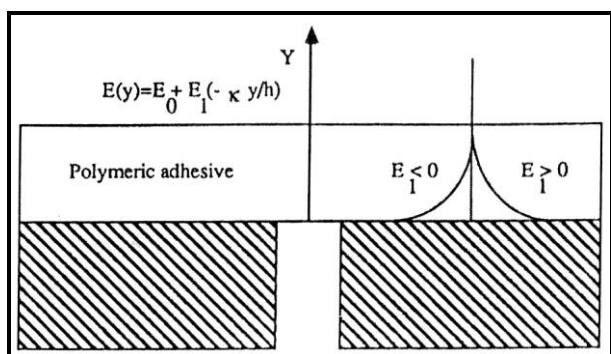


Figure 2. Schematic showing modulus gradient normal to the interfacial junction.

Several methods are used in practice to achieve enhanced interfacial interaction such as reduction in surface tension of the PU, introduction of bonding agents in the system and the like. A recent technique that may influence the bond quality relies on the selective variation of modulus normal to the PU-substrate junction, as shown schematically in Fig. 2. The principle first applied by this author to flat interfacial assemblies showed that varying the modulus normal to the PU-adherent boundary could indeed augment bond strength [6]. It seems desirable to relate the above results to practical systems, where the particles are embedded in the continuum of the bulk PU matrix. The present paper is a work in that direction.

2. Materials and Methods

2.1 Materials

A Diorez PRI/Isonate 143L PU supplied by McPherson Polymers (Bury, UK) was used. Diorez PRI is diethylene glycol adipate polyester with a molecular weight of c. 2000. Varying the amount of phenyl mercuric salt catalyst (Thocrat 535) alters the reactivity of the PU forming reaction. Isonate 143L is methylene diphenyl diisocyanate (MDI) of equivalent weight c. 143. The MDI/polyester were mixed in the 1:5 weight ratio. 1-4, butane diol supplied by Aldrich was used as the chain extender.

2.2 Film fabrication

Microscopy of the structural domains is best performed from a THF cast film of the fully reacted PU. A method that was found useful was transferring a small quantity of the mixed liquid components to the plate of a Weissenberg rheogoniometer under constant rotation and *in situ* curing of the resultant film in the environmental chamber at 60°C for one hour. A schematic of the cone-plate assembly with an exaggerated cone angle indicating the stress regime appears in Fig 3.

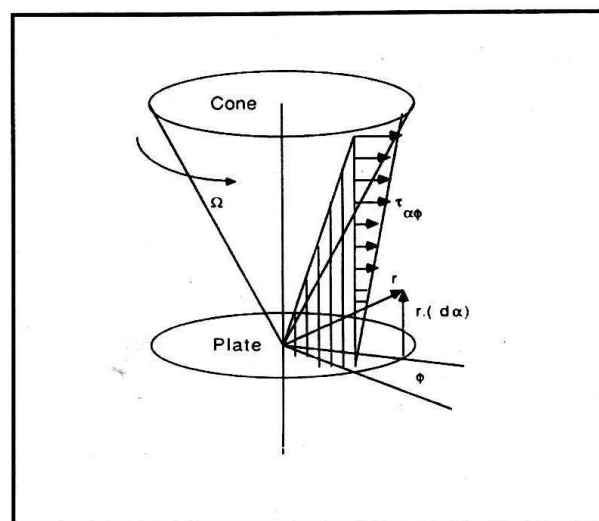


Figure 3. Schematic of the cone and plate assembly for film fabrication.

2.3 Fabrication of micro-composites

Viscous reactive mixing of the components was performed using the standard procedure involving programmed sequential addition of particles to the PU reactant mix, casting into an evacuated mould (Fig. 4) and curing at 60°C for several hours [7].

The particle size varied in the 20 to 200 micron range. Two types of micro-composites were fabricated using virgin and resin-coated particles respectively. For the latter case, the method of preparation employs particle coating that allows a modulus gradient at the particle-matrix interface. The procedure is proprietary and is currently the subject of a patent application.



Figure 4. Mould assembly used to fabricate micro-composites with clamping studs in place.

2.4 Scanning electron microscopy

The cured micro-composite specimen exhibited a glass transition temperature (T_g) of c. -60°C as determined by DMTA, and were easily fractured in liquid nitrogen. Morphology investigation was made by scanning electron microscopy (SEM). The SEM micrographs were taken on gold-sputtered fracture surfaces produced under liquid nitrogen.

2.5 ATR-IR spectroscopy

Attenuated total reflection infrared spectroscopy (ATR-IR) was performed on a Perkin-Elmer instrument on fully reacted PU. The PU was placed above a KBr crystal base, which served as a beam retainer/reflector. The incident IR probed the sample surface and was directed to the detector system by a mirror arrangement [8]. In the partially reacted case, a thin film of the mixed liquid sample was spread on the KBr crystal and simply placed in the sample holder for transmittance of the beam to the detector.

3. Results and Discussion

3.1 Nano-polymer

Micrographs of the fully reacted polymer film appear in Figs. 5 and 6. Phase segregation is clearly apparent. The microstructure is characterized by hard block spheroidal globules (HSG) and hard segment spherulites (HSS). The

amorphous or featureless regions are therefore those of the soft segment. They can crystallize under extensive micro-phase segregation as detected by X-ray diffraction at an angle of incidence of c. 12° [9].

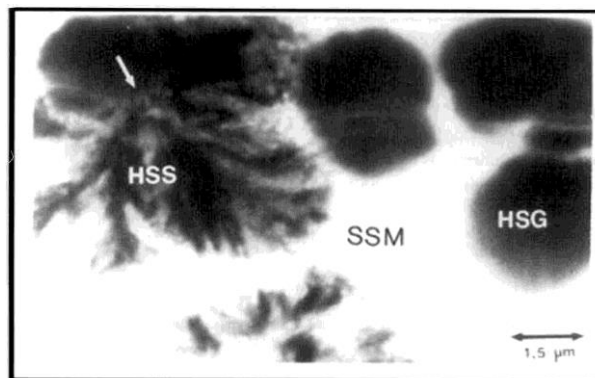


Figure 5. Micrograph of the phase-segregated PU nano-polymer showing various hard block structures.

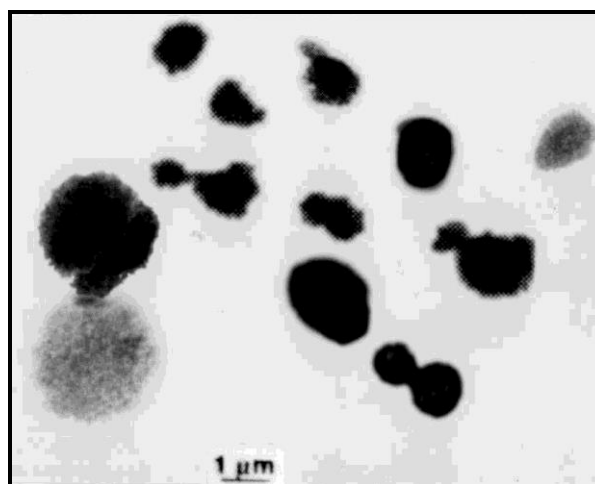


Figure 6. Micrograph of the phase-segregated PU nano-polymer showing hard segment spheroids.

ATR-IR/FT-IR has been previously employed to assess the onset of nano-segregation phenomenon [9, 10]. Fu et al. [10] carried out IR spectroscopy for the entire three major precursors polymer chains i.e., butadiene, polyester and polyether, and found phase-segregation as revealed by an enhanced $-\text{NH}$ stretching peak at 3320 cm^{-1} . A segment of the IR for the present case appears in Fig. 7. This is the important carbonyl region at c. 1750 cm^{-1} . The entire spectrum was reported earlier [8] and is not reproduced. A shift in the carbonyl peak is evident. When urethane hard segments associate with each other, hydrogen bonds form between the carbonyl oxygen and the amine hydrogen [11,12]. This results in the frequency shift in the $\text{C}=\text{O}$ peak

as illustrated in Fig. 7. During polymerization the C=O peak increases as isocyanate groups [-NCO] convert to urethane [-NHCOO]. It is this association of hard segments that leads to the observed micro-phase segregation, which by and large determines the dynamic viscoelastic properties of the PU e.g., loss modulus and the damping coefficient, $\text{Tan } \delta$.

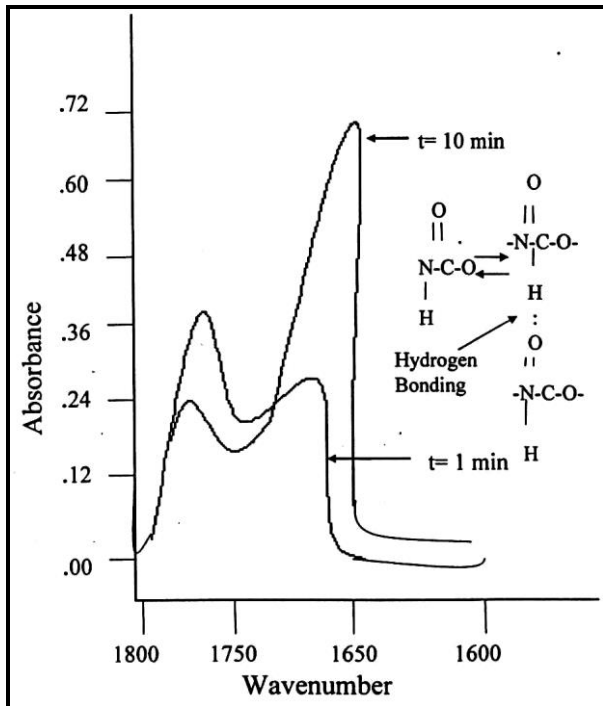


Figure 7. ATR-IR spectrum of the partially and fully reacted nano-polymer indicating shift in the carbonyl peak.

3.2. Novel micro-composite

Fig. 8 depicts the SEM of fractured micro-composite employing resin-coated particles, while Fig. 9 shows the same for the unmodified virgin particles. The difference in the morphology is quite succinct. In the modified composite, the particles are seen to reside securely in the interstices, without any particle pullout. On the contrary, the fragile nature of the particle-matrix interface is quite apparent in case of unmodified composite. It is important to note that the observed improvement in the interface strength is obtained without incurring any processing penalty. In the bonding agent-doped systems as described below, the increase in the concentration of polar groups works to the detriment of rheology. No such tendency was observed in the modified-particle micro-composite.

A property that affects the mechanical response is the strain amplitude dependence (m) of the

shear modulus (G) of highly filled composites. In essence this means that on stretching under applied stress, these materials exhibit a non-linear behavior i.e., a plot of loss modulus vs. strain shows a non-linear character, primarily due to dewetting of the particles during the extension process. An increased interaction at the polymer-particle interface as observed in SEM of Fig. 8, should serve to suppress this non-linear behavior defined by Eq. 1 below [13]:

$$m \sim \log [G d/f \phi(1-\phi) \delta] \quad (1)$$

Where “ m ” is the degree of non-linearity. Indeed “ m ” is seen to decrease with smaller particle diameter, d , and higher cohesive energy density, δ . In conventional systems, δ assumes values of 25 and 17 mJ/m^3 for the strong and weak interface respectively.

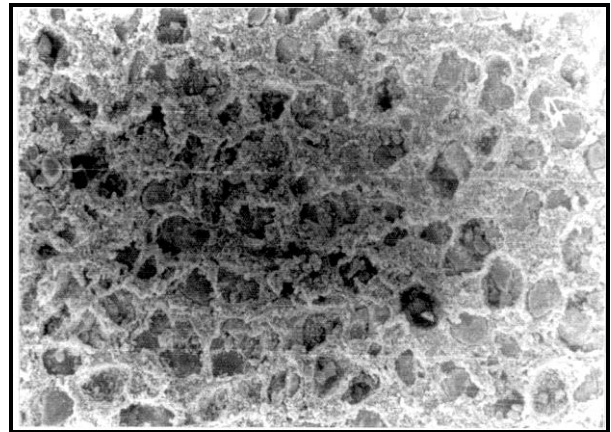


Figure 8. SEM of the fractured micro-composite employing modified particles.

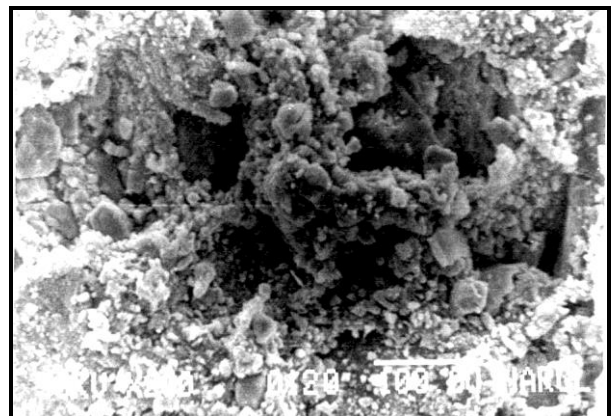


Figure 9. SEM of the fractured micro-composite employing virgin particles.

The securing of particles in the modified composite, without interfacial fracture (Fig. 8), is

qualitatively synonymous with increased adhesion and reduced non-linear index m . Thus m takes on the physical significance of a molecular slippage factor, which should decrease with increased interfacial attraction. Of course, the PU matrix plays the central part in conferring viscoelastic character to the composite, especially at low temperatures and high strain rates. Temperature bound lies from -20 to 75°C , while these systems are expected to exhibit a minimum strain c. 45 % at ambient and 15 % under high strain rates (10 m/min) conditions.

3.3. Parallel work on micro-composites and interface morphology

The strain capability of a micro-composite may be increased by an improved interaction between the polymer and the particles through bonding agents, or through surface modification of the particles. Bonding agents are bipolar compounds that induce H-bonding at the polymer-particle interface, thus forming chemical bridges with debond energy in the c. 40-100 KJ/mol ranges. Amines, aziridines, and ferrocenes are the three generic classes as elaborated in reference [5]. Conventionally, surface modification relies on the introduction of specific functional groups, capable of enhanced physical or chemical interaction with the polymer chains/end groups. The mechanism of an amine type-bonding agent is shown in Fig. 10. Preparation of reactive filler particles to obtain terminal OH functional groups is a fine example of this approach, as depicted in Fig.10. The $-\text{OH}$ can react with the $-\text{NCO}$ in the urethane matrix to produce urethane junctions:



The particles are thus linked to the host polymeric matrix through covalent urethane linkages (c. 40-100 KJ/mol), Eq. 2, rather than through simple physical contact, in which case the debond fracture energy is derived only from the thermodynamic work of adhesion that is typically small (c. 0.40 KJ/mol).

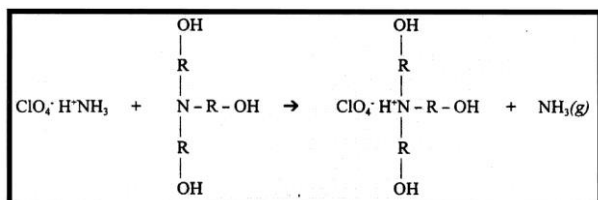
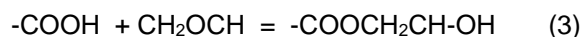


Figure 10. Interaction of an amine bonding agent with an AP particle to yield surface OH functional groups.

The securing of particles or indeed fibrous inclusions to host polymeric matrices is not without engineering precedence. In fact much of the earlier work originates from well-established polymer engineering practice [14]. Liquid crystalline polymer-PET blend and the rubber-toughened epoxy is a patent case in point [15,16]. The interface in the LCP-PET combination comprises spherical LCP particles residing in the PET matrix, albeit through plain physical contact. Consequently, the interface is quite fragile and the particles pop out of the matrix following fracture [15]. Contrarily, in the carboxyl rubber-epoxy system, the interfacial bond strength is augmented by direct covalent bonding between the carboxyl $[-\text{COOH}]$ domains and the epoxy $[\text{CH}_2\text{OCH}]$ matrix:



The resulting bond is so strong that it is impossible to dislodge the particles even by tearing the specimen [16].

4. Conclusions

1. The nano-material microstructures together with the material interface are important structural elements of the fabricated micro-composites. However, for given matrix properties, the entire edifice of the composite assembly lies in the integrity of the interfacial junction.
2. The principle of modulus gradient has been successfully extended to a continuum system in which the substrate (particles) resides in the PU adherent matrix. The modified PU-particle system combines the ease of processing with improved strength at the interfacial junction.
3. SEM clearly demonstrates the vastly different interfacial morphologies obtained for the conventional untreated system and the one incorporating modified particles.
4. An increased adhesion at the interfacial junction as observed in the SEM should serve to augment the mechanical properties of the modified micro-composite. On the other hand, the morphology of the nano-material micro-matrix may be tailored to tune the viscoelastic response in the fabricated system.

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References

- [1] L.N. Philips and B.B.V. Parker, "Polyurethanes, Chemistry, Technology, and Properties", The Plastic Institute, London (1984).
- [2] M.B. Khan, International Seminar & Workshop on High Temperature Materials for Industry & Development of Indigenous R & D Capability, convened jointly by Pakistan Science Foundation and European Technology Development Ltd., UK under the auspices of Pakistan Materials Research Society at Islamabad, 19-20 Dec. (2005).
- [3] A. Mateen, J. PIChE, **19/20**, No. 1-4 (1991-92) pp. 37.
- [4] J.B. De Vries, Proceedings of the First International Congress on Compatibilizers and Reactive Polymer Alloying, New Orleans (1989) pp. 41.
- [5] M.B. Khan, in Handbook of Engineering Polymeric Materials, N.P. Cheremisinoff, Ed., Marcel Dekker, N.Y (1997) p. 705.
- [6] M.B. Khan and B.J. Briscoe, Polym. Composites, **15**, No. 1 (1994) 83.
- [7] M.B. Khan, J. PIChE, **26**, No.1-2 (1997) 25.
- [8] M. B. Khan and B.J. Briscoe, 12th International Def. Sci. & Technol. Seminar, Wah Cantt, Nov. 30 – Dec. 2, (1992) p. 107.
- [9] B.J. Briscoe, M.B. Khan and S.M. Richardson, J. Adhesion Sci., Technol., **13**, No.6 (1989) 487.
- [10] B. Fu, W.J. Macknight and N.S. Schneider, Rubb. Chem. & Technol., **69** (1987) 896.
- [11] M.M. Coleman, K.H. Lee and P.C. Painter, Macromol., **19** (1986) 2149.
- [12] E. Yilgor, E. Yurtesever and I. Yilgor, Polymer, **43**, No. 24 (2002) 6561.
- [13] R.G. Stacer and M. Husband, Prop. & Expl., **16** (1991) 167.
- [14] L.E. Nielsen and R.F. Landel, "Mechanical Properties of Polymer Composites", 2nd Edition, Marcel Dekker, N.Y (1994).
- [15] G. Poli, M. Pasi, and F.P. La Manta, Polym. Engg. Sci., **36**, No. 9 (1996) 1244.
- [16] G. Davey, S. Hashemi and A.J. Kinloch, International J. Adhesion and Adhesives, **9**, No. 2 (1989) 9.