PHYSICAL TRAINING METHODS FOR MINE RESCUERS IN 2015

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Abstract: Research and development activities presented were aimed at obtaining a nanocomposite polyurethane matrix with special anti-wear, anti-slip and fire-resistant properties. Research and development works were materialized by obtaining polyurethane nanocomposite matrix, by its physico-chemical modification in order to give the desired technological properties and by characterization of the obtained material. Polyurethane nanocomposite matrix was obtained by reacting a PETOL 3 type polyetherpolyol (having a molecular weight of 5000 UAM) with a diisocyanate under well-established reaction conditions. Target specific technological properties were obtained by physical and chemical modification of polyurethane nanocomposite matrix. The final result was getting a pellicle material based on modified nanocomposite polyurethane, with anti-wear, anti-slip and fire-resistant properties, compatible with most substrates encountered in civil and industrial construction: wood, concrete, metal.

Key words: polyurethane, nanocomposite, antiwear, antislip, fire resistant

Introduction

A nanocomposite represents a multiphase solid material in which the disperse phase has one, two or all three dimensions of the order of magnitude less than 10^{-9} m. Polymeric nanocomposite may be defined as a material with polymeric matrix in which a nanofiller with the $\max. 100 \times 10^{-9}$ m particle size is dispersed. Reinforcing materials can be grains, strips (e.g. phyllo-silicates type clays) or fibers (e.g. carbon fiber nanotubes). Polyurethanes belong to reaction polymers class and are obtained by polyaddition reaction occurring between a polyol - hydroxyl (OH) and a polyisocyanate ($-N = C = O$), in the presence of a catalyst and of other additives. The nano- component represents that component of the recipe that allows the construction of intercalated molecular structure of the composite- is represented by a layered aluminosilicate - montmorillonite – phyllo-silicates type. This mineral has a layered molecular structure that allows intercalation or construction of other organic macromolecules between two successive layers of constituting atoms chains, in order to obtain a nanocomposite. Lamellar/layered montmorillonite structure allows self-construction of polyurethane macromolecule through successive layers and as well as their embedding as a result of polyurethane macromolecule growth. Getting polyurethane nanocomposite matrix occurs after the polyaddition reaction between a diisocyanate, i.e. 4,4-diisocyanate diphenylmethane (MDI) with equivalent -NCO groups (identical reactivity) and a polyether polyol, i.e. 3 PETOL 36 3 BO modified with 6wt. % montmorillonite. Tests on polyurethane matrix revealed a significant improvement in their physical properties, particularly in thermal resistance.

2. Nanocomposites classification

Ceramic matrix nanocomposites are those nanocomposites for which most of the volume consists of the ceramic block in which metal oxides, nitrides, borides are dispersed at nanoscale.

Metallic matrix nanocomposites are those nanocomposites based on metallic materials reinforced using various agents. Metal matrix / carbon fiber nanotube represents well known metal nanocomposite. It is also used together with carbon fiber or boron nitride, silicon carbide to obtain metallic nanocomposites.

Polymer matrix nanocomposites are those nanocomposites for which the matrix containing distributed the nanofiller consists of a polymer. Depending on how much inorganic phase is dispersed in the polymer matrix, nanocomposite structure can be either exfoliated or intercalated.

Fig.2.1. Reinforcing agent (ceramics) 1, polymer matrix 2

Fig.2.2. Intercalated nanocomposite 1, exfoliated nanocomposite 2

3. Obtaining polyurethane nanocomposite - anti-wear, anti-slip and fire-resistant coatings based polyurethane nanocomposite

Polyurethanes are a versatile type of polymers capable of meeting the requirements of a wide range of technical and industrial applications.

Synthesized by the reaction of a polyisocyanate and a polyhydroxy compound, the polyurethanes offer the advantage that, by appropriate selection of raw materials, of reactants ratio, one can modify the polymer properties from elastomer stage to high-cross-linked resin stage. To improve certain properties (stiffness, heat resistance and fire resistance) and / or to reduce cost, polyurethanes are reinforced with various fillings: calcite, micronized quartz, clays.

However, use of conventional fillers results in a decrease in polymer flexibility and, over time, can induce cracks in the material mass. Polyurethane matrix nanocomposite is a new material, obtained by a modification process of polyurethane matrix with a chemical species having a special molecular structure that allows the construction and the subsequent development of macromolecules (polyurethane macromolecules in the present work) between its interstitial spaces.

The use of layered silicate type nanoscale fillers improves the mechanical properties, thermal stability and fire resistance without significant alteration of the matrix flexibility. The properties enhancement is directly related to the degree of filler dispersion in polyurethane matrix, the best results being obtained for nanocomposites having exfoliated and intercalated intermolecular structure.

3.1. Synthesis of polyurethane nanocomposite matrix required for anti-wear, anti-slip and anti-fire coating products to be used in civil and industrial buildings floors

Polyurethanes belong to the reaction polymers class, being obtained by a polyaddition reaction between a polyhydric alcohol (polyol) and a polyisocyanate in the presence of a catalyst and of other additives.

Polyisocyanate is an organic compound molecule having a number greater than or equal to two isocyanate groups in its molecule in order to achieve macro-chain development. Polyol is an organic compound that has in its molecule a number of OH groups equal to or greater than two, for the same reasons.

Fig.3.1.1. Scheme of polyaddition reaction –OH / -N=C=O

To synthesize the polyurethane matrix various raw materials have been used, each of them corresponding to one component of the reaction scheme for the preparation of the polyurethane matrix. Basically, two-component polyurethane consists of a polyol component comprising the other elements of the recipe and of a isocyanurate component comprising only the diisocyanate involved in crosslinking.

1. Polyol component is a complex mixture containing the following elements in a well-established stoichiometry:

- **a polyetherpolyol 3** obtained from the polyaddition reaction occurring between propylene oxide and glycerol. Thus obtained polyether polyol is a polyol having molecular weight of approx. 5000 UAM. It is provided by Oltchim under the name PETOL 36 3 BR. It is a product that contains only primary hydroxyl groups and exhibits high reactivity. The product is not toxic and does not require any special occupational safety. It is a clear, colorless, viscous liquid.

Fig.3.1.2. Structure of PETOL 36 3 BR polyol molecule

- **- an adhesive properties resin** belonging to esterified colophony category, HE PENTALYN type, melting point 114 °C, provided by MAGITECH Bucharest. The use of this resin is aimed at enhancing the composite adhesion to surfaces it is applied.
- **a specific catalyst** for polyaddition chemical reaction, Sn^{2+} octoate, Pb^{2+} octoate, MERCK supplier
- **a reinforcing component** of the composite. Micronized silica (quartz) was used as reinforcement. Its physical and chemical properties were decisive for its choice. Thus, micronized SiO_2 has high hardness, high polarity which makes it fully compatible with polar polyurethane matrix and zero chemical reactivity.
- **flame retardant component** is that component which gives self-extinguishing properties.
- **the recipe dispersion medium** is an organic solvent compatible with all constituents of the composition

2. Nano component – that recipe component that enables obtaining intercalated molecular structure composite - is represented by a layered aluminosilicate - montmorillonite – phyllosilicates category. This mineral has a layered molecular structure, which allows for intercalation or building of other organic macromolecules between two successive macromolecule constituent atom chains, to obtain a nanocomposite. Lamellar/layered structure of montmorillonite allows self-building of polyurethane macromolecule through successive layers, as well as, their incorporation as a result of polyurethane macromolecule growth. The occurrence of OH groups in the structure of montmorillonite leads to the development of chemical bonds between organic macromolecule and nanofiller

Fig. 3.1.3. Layered molecular structure of montmorillonitului

3. Isocyanates component is 4,4 'methylene diphenyl diisocyanate (MDI). This is a symmetric diisocyanate with chemical formula presented in fig.2.1.4

Fig. 3.1. 4. Molecular structure of MDI

MDI is toxic and dangerous product that requires which requires adherence to specific rules of occupational safety and wearing of appropriate protective equipment.

3.1.2. Modification of PETOL 36 3 BR polyol with montmorillonite in order to obtain nanocomposite polyurethane matrix

Nano-polyol component is obtained by modifying the initial PETOL 36 3 BR polyol with layered aluminosilicate montmorillonite type. Afterwards, this component, modified as above mentioned, becomes reagent in the polyaddition reaction with MDI diisocyanate to obtain a nanocomposite polyurethane matrix. PETOL 36 3 has a high molecular weight of 5000 UAM, revealing a long aliphatic branch- 110-120 atoms. This structural attribute makes it suitable for the subsequent polyurethane

The research work showed a good compatibility between PETOL 36 and montmorillonite. It can incorporate up to 6 wt. % montmorillonite, without changes in their physicochemical properties and / or without containing solid waste at the end. The PETOL 36 polyol modified with 6% gravimetric parts of montmorillonite was subsequently stoichiometrically crosslinked with diisocyanate to obtain nanocomposite polyurethane matrix.

Depending on the amount of isocyanate which reacts with the polyol, weaker or stronger crosslinked polymers are yielded. Stoichiometrically, for complete cross-linking, 3/2 moles of MDI are used relative to 1 mole of PETOL 36. In practice, it was added an amount with 15% higher than strictly necessary in terms of stoichiometry to offset any isocyanate groups losses which are involved in intramolecular addition reactions or in reciprocal polymerization reactions. As a result of a polyaddition reaction, it was finally obtained a nanocomposite polyurethane macromolecular structure, as shown in Fig. 3.1.7. Based on the control of rheological parameters - dynamic viscosity respectively - optimal recipes, in terms of used isocyanate and of the reaction catalyst, were chosen.

The obtained nanocomposite polyurethane matrix was characterized by a series of thermal gravimetric tests to investigate its thermal stability. From TGA/DTG curves (fig.3.1.8), one may notice that modified polyol with 6wt % montmorillonite shows substantially improved thermal stability as compared to a typical polyurethane matrix obtained using unmodified polyol.

From fig. 3.1.8., one may notice that for the polyurethane obtained with pure polyol (1) the first weight loss occurs at 289,3°C. It may be also observed that at 380,6 °C, corresponding to the most

pronounced decomposition process (decomposition temperature), the weight loss represents 93.46% of the initial weight. DSC curve corresponding to the polyurethane obtained using modified polyol with 6 wt% montmorillonite (2) shows that the first weight loss occurs at 317,0°C.

At this temperature the weight loss is only 14%. At the same time, only at 397,7°C decomposition occurs more pronounced and it does not exceed 67.02% of the initial weight. For pure polyol total degradation product occurs at 380,6°C, whereas for modified polyol, at 397,7 °C, decomposition occurs only for 81.21% (14.19 + 67.02) of the initial amount. These thermograms prove that it was obtained a polyurethane matrix with enhanced thermal stability determined by the nano-modification process.

3.2. Making anti-wear coating

To rigorously cover the stages required for a technology development from a research process, an itinerary of research work is mandatory.

Thus, at first, the sources of raw materials, the laws under which the work is performed to characterize the raw materials and the obtained products were identified. It was also identified how to work and experiments with the obtained product were conducted.

An anti-wear coating must meet several technological requirements in terms of their features, referring either to intrinsic characteristic or to properties that may be acquired through a subsequent modification. Improved mechanical properties and enhanced thermal stability are conferred by nano-modification polyurethane matrix.

Self-extinguishing characteristics were provided by adding hydrated alumina coating composition in combination with halogenated paraffin.

Anti-slip properties were provided by surface coating modification, performed at a certain moment of the pot life with a granular super hard material (SiC, also known as carborundum, fig.3.2.1).

Fig. 3.2.1. Optical microscopy image(x 30) of granular carborundum

The surface modifier, grained carborundum SiC (average grain size of 0.7 mm), used to give anti-wear and anti-skid properties, was embedded in the polymeric material surface.

Fig. 3.2.2. Dynamic viscosity variation in time for PETOL 36- MDI mixture (optimum receipe) during „pot – life”

From Fig. 3.2.2, one may notice that the dynamic viscosity variation in time is not linear. There is an induction time of the polyaddition reaction of about 16-20 minutes, during which the viscosity change is not significant. After about 16-18 minutes, mixture viscosity starts to increase, at the beginning with a reduced slope and then it exponentially increases until the solid state is reached. Viscosity change from liquid to solid occurs in approx. 30 minutes from the moment of mixing the polyol component with isocyanate component. This time is generically termed "pot life" and represents an important technological indicator for all two-component materials and it represents also the machinability time of the material.

From viscosity variation diagram the optimal time for surface modification with anti-wear coating item may be also determined. The viscosity of the material deposited as a film on the surface that protects must be low enough to allow anchoring of anti-wear granular material as a result of its adhesive properties, but at same time to be enough high so that the grains of modification material not to sink in film mass fig. 3.2.3.-1. In the determinations, it was found that the optimum time for film surface modification with anti-wear material is when the viscosity of the mixture begins to increase (19-23 minutes from the time of mixing components) .After approx. 2-3 hours, the coverage (Fig. 3.2.3.-2) can be brought into operation.

Fig. 3.2.3. Anti-wear (1) and anti-slip (2) coating based on polyurethane nanocomposite

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