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In situ Polymerisation of Urethane-Urea Copolymers for Tuff Consolidation

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Summary: two different diisocyanates were investigated as co-monomers for *in situ* polymerisation of poly(urethane-urea) into Neapolitan yellow tuff for conservation and restoration purpose. The obtained copolymers were characterised by means of FTIR spectroscopy, whereas the protective and consolidating efficiency of the performed treatments was evaluated through water capillary absorption, water vapour permeability and abrasion resistance measurements. The distribution and the penetration depth of the synthesized copolymer were also analysed applying micro-FTIR. The morphology of treated tuff was investigated by SEM. It was shown that comparatively higher protective and consolidating properties are achieved by using 1,6-diisocyanatohexane as monomer for *in situ* polymerisation.

Keywords: consolidant; *in situ* polymerisation; polyurethane; protective; tuff

Introduction

Many conservators and restorers experimented polymeric materials as consolidating and protective agents for stone restoration usually applying them on stone surface by brush, spray, pipette, or by immersion. The treatments effectiveness strongly depends on macromolecules deep penetration [1], which is also affected by substrate characteristics, such as porosity, pore size, surface polarity, properties of the consolidating solution, and application method. *In situ* polymerisation of monomers for restoration of stone artefacts proved to be a valid alternative [2, 3] to the above mentioned application methods; to increase polymer penetration depth monomers are carried and then polymerised inside the stone.

For conservation and restoration purpose in a previous work [4, 5], the first *in situ* polymerisation of poly(urethane-urea) inside stone substrate was set up, as polyurethanes have excellent properties, such as mechanical strength, abrasion resistance, adhesive properties, impact resistance and flexibility [6, 7], easily controlled by appropriate choice of reagents and relative amount. The ratio between co-monomers, the catalyst and its concentration was optimised in order to increase the extent of the isocyanate-polyol reaction. Furthermore it was demonstrated [5] that through *in situ* polymerisation of

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poly(urethane-urea) a noticeable penetration depth of the synthesised material inside the stone is achieved together with a suitable polymer amount absorbed at the end of the treatment.

In this work two different diisocyanates were used as monomers for the *in situ* polymerisation reaction. The co-polymers obtained inside stone were characterised in order to establish the urethane/urea ratio. Moreover relationship among copolymers distribution and related morphology, as well as effects of the performed treatments on tuff properties were investigated.

The monomers selected were polypropylenglycol, isophorondiisocyanate and 1,6-diisocyanatohexane; catalyst was zirconium acetylacetonate; stone was Neapolitan yellow tuff; the reactions were carried out at room temperature in order to reproduce the environmental operative conditions of conservators.

Experimental

Synthesis

Polypropylenglycol (PPG, $M_W = 425$), isophorondiisocyanate (IPDI, $M_W = 222.29$), 1,6-diisocyanatohexane (DIE, $M_W = 168.20$), 1-methyl-2-pyrrolidinone (NMP), and zirconium acetylacetonate (ZrAcAc) were purchase from Aldrich; acetone (99.8%) was obtained from Lab-scan. All the materials were used as received except for PPG which was dried under vacuum overnight at 50°C. Neapolitan yellow tuff (Pozzuoli, Napoli) was cut in samples of 5x5x2 cm.

Two following polymerisation solutions were prepared:

a) IPDI and PPG (molar ratio 1/1) were dissolved in acetone; ZrAcAc was used as catalyst using the ratio $[ZrAcAc]/[-NCO] = 3.3 \times 10^{-3}$ mol/mol.

b) DIE and PPG (molar ratio 1/1) were dissolved in acetone; ZrAcAc was used as catalyst using the ratio $[ZrAcAc]/[-NCO] = 3.3 \times 10^{-3}$ mol/mol.

The dry content (i.e. weight of mixture of monomers and catalyst) was kept at 40% (wt/wt) by adding the right amount of acetone. The *in situ* polymerisation reactions were carried out on tuff samples as already described [4]. Samples codes were respectively Z (tuff samples treated by the mixture a) and D (tuff samples treated by the mixture b).

Characterisation

The amount of synthesised polymers into the stone was measured by means of thermogravimetric analysis (TGA). Measurements were performed with a Perkin Elmer Diamond Thermogravimetic/Differential Thermal Analyzer; the heating rate was 10°C/min in the temperature range 50 - 600°C in nitrogen flow.

The molecular characterisation of the polymeric materials synthesised inside stone was performed by means of Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra of the materials extracted from treated stone samples in 1-methyl-2-pirrolidynone (NMP) and cast directly on KBr disks were collected by a Perkin Elmer spectrometer (Paragon 500) in a range of 4000 - 400 cm^{-1} using 32 scans summation and a nominal resolution of 4 cm^{-1}.

The distribution of the synthesizes polymers along the cross sections of tuff samples was investigated by means of Fourier Transform Infrared Microscopy (Micro-FTIR), using a Perkin Elmer AutoIMAGE FT-IR Microscope System - Spectrum GX. The microscope was used in reflection mode, with 300 scans recorded for each spectrum and a nominal resolution of 4 cm^{-1}.

The morphology of the synthesised polymers was investigated analysing untreated and treated tuff samples by means of a Philips XL20 Scanning Electron Microscope. All samples were mounted on carbon stubs, coated with gold-palladium and observed at 30 KeV.

The consolidating and protective effectiveness of the treatments performed was evaluated by measuring the water capillary absorption [8], the permeability to water vapour [9] and the abrasion resistance.

Results and Discussion

Relative amounts of synthesised polymers were determined by measuring the weight loss due to the degradation process of the polymer, calculated by subtracting the TGA trace of untreated tuff to the traces of the treated tuff samples (% weight loss). The percent relative amounts of Z and D polymers were 9.9 % and 10 % respectively.

The molecular characterisation of the synthesised co-polymers were performed by means of FTIR analysis. In Figure 1 typical FTIR spectra of the synthesized polymers, after extraction from tuff samples in NMP, are reported in the range 1800 – 1400 cm^{-1}.

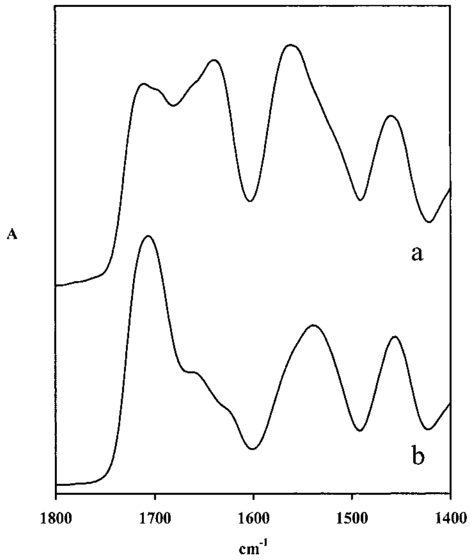

Figure 1. FTIR spectra of synthesised polymers: a) Z sample; b) D sample.

As it can be observed, experimental data for both the two experiments show the formation of polyurethane: in the region between 1750 – 1600 cm^{-1}, characteristic absorption bands of urethane bonds centred at ~1714 cm^{-1} (free C=O) and ~1687 cm^{-1} (bonded C=O), although partially overlapped, are distinguishable from bands of urea bonds centred at ~1665 cm^{-1} (free C=O) and ~1640 cm^{-1} (bonded C=O). The area values of the above reported absorption bands were calculated through deconvolution process and Gaussian fitting carried out by means of the software Thermogalactic Grams/AI 7.01. The values of ratio (R) between the area of the absorption bands assigned to urethane and urea groups respectively [4, 10] are reported in Table 1.

Table 1. Ratio R between the area of the absorption bands corresponding to the C=O stretching of urethane and urea groups.

Sample	R (± 5%)
Z	0.79
D	2.84

As it can be observed, by using for the *in situ* polymerisation reaction DIE as co-monomer in place of IPDI, the urethane groups remarkably increase in respect to urea groups.

The distribution of the poly(urethane-urea) synthesised inside tuff samples was evaluated analysing the cross sections of untreated and treated samples by means of Micro-FTIR. The spectra were collected along the direction (d) parallel to that of capillary rising of the monomers, on investigated areas of 300 μm^2 for each point, at distances of about 3 mm along d among the investigated points. With this technique it is possible to evaluate the differences between the areas of the CH_2 stretching absorption bands that can be related to the amount of polymeric material synthesised inside the stone. Spectra were transformed by applying the Kubelka-Munk function used to describe diffuse reflectance [11]. In Figure 2a and 2b the area values of the CH_2 stretching absorption bands vs. the distance parallel to the capillary rising direction of the monomers (d) for the samples Z and D are respectively reported.

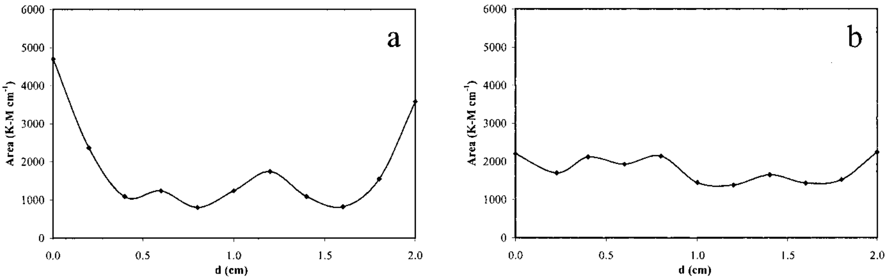

Figure 2. Area values of CH_2 stretching absorption bands as a function of distance d from the surface of application: a) sample Z; b) sample D.

As shown in Figure 2a the poly(urethane-urea) synthesised using IPDI as co-monomer is not well distributed inside the tuff because a material surplus is observed on the external sides of the sample. On the contrary the homogeneous distribution of the polymer synthesised using DIE is shown in Figure 2b.

In Figure 3a and 3b typical SEM micrographs of surfaces of tuff samples untreated and treated with D are respectively reported. As shown in Figure 3a it is possible to observe the presence of pseudocubic chabasite and prismatic phillipsite crystals, main constituents of Neapolitan yellow tuff [12]. The synthesised poly(urethane-urea) forms homogeneous and regular films that don't modify the morphological features peculiar to the tuff crystals as it can be observed in figure 3b. The same results are observed for Z sample.

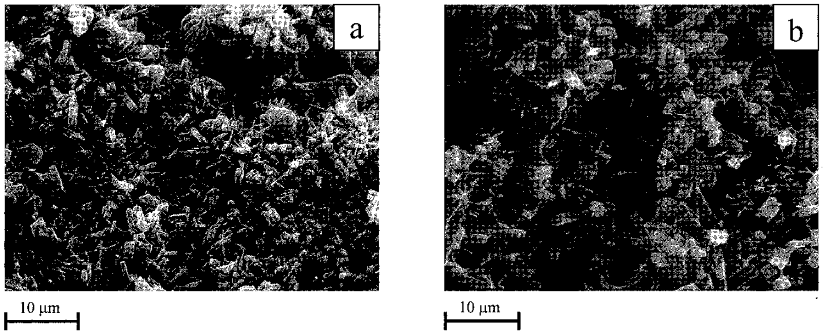

Figure 3. SEM micrographs of: a) untreated tuff; b) D sample.

The protective properties of the *in situ* polymerised copolymer were estimated by measuring the amount of absorbed water per surface unit of the tuff samples (A (g/cm^2)) vs. time ($t^{1/2}$ ($sec^{1/2}$)). The capillary absorption coefficient, CA (g cm^{-2} $t^{-1/2}$) was measured by initial slope of the curves. In Figure 4 the capillary absorption curves are reported for untreated tuff, Z and D samples.

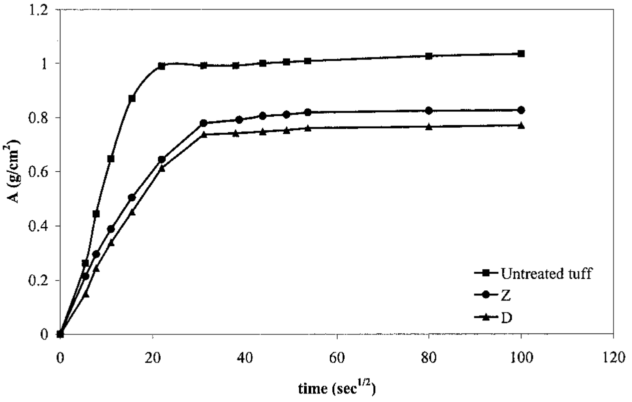

Figure 4. Capillary absorption curves for untreated tuff, Z and D samples.

The values of water capillary absorption are reported in table 2.

Table 2. Main values of capillary absorption coefficient CA of untreated and treated samples.

Sample	CA (g cm^{-2} t$^{-1/2}$)
Untreated	0.0548 ± 0.0046
Z	0.0318 ± 0.0009
D	0.0300 ± 0.0009

Concerning untreated tuff, the water absorption is very high and the maximum value of absorption is reached already during the first 8 - 10 min of testing; this is due to the extremely high porosity of tuff material. Z and D samples absorb water slowly than untreated sample. The values of CA are similar for both the treated samples and smaller than untreated tuff, thus indicating that performed treatments confer a effectiveness protection to the stone.

In Table 3 mean values of permeability to water vapour of untreated and treated tuff are reported. Permeability (g/m^2·24h at 20°C) is expressed as the ratio between the weight variation of the whole system in 24 hours and the sample surface.

Table 3. Mean values of permeability to water vapour of untreated and treated samples.

Sample	Permeability (g/m^2·24h)
Untreated	384.45 ± 1.5
Z	240.30 ± 3.7
D	197.54 ± 4.3

From data reported in Table 3 it is possible to observe that the performed treatments reduce the permeability in respect to the untreated sample. Nevertheless this reduction is enough low to ensure that treated samples are still permeable to water vapour.

Untreated and treated tuff samples were undergone to abrasion tests carried out by means of Taber Linear Abrasion Tester Model 5700. Each sample was abraded by performing 200 runs at 15 runs/min, under a weight of 350 g. The aggregative efficacy was determined following the formula:

$AE\% = 100 \times (\Delta M_{untr} - \Delta M_{tr}) / \Delta M_{untr}$

where ΔM_{untr} is the average difference in the untreated samples between the weight values before and after 200 abrasive runs; ΔM_{tr} is the difference between the initial weight and the weight after 200 abrasive runs measured for each treated sample.

In Table 4 mean values of AE% are reported.

Table 4. Mean values of AE% of untreated and treated samples.

Sample	AE%
Untreated	0
Z	28.2
D	41.3

It should be noted that both the performed consolidating treatments show high aggregative efficacy. Moreover the extent of the aggregative effect is higher for the polymer synthesised by using DIE as a co-monomer.

Conclusions

In situ polymerisation of two poly(urethane-urea) was carried out using polypropylenglycol (PPG) and 1,6-diisocyanatohexane (DIE) or isophorondiisocyanate (IPDI) as co-monomers, and zirconium acetylacetonate as catalyst. FTIR analysis of the two copolymers so synthesized shows that DIE is a diisocyanate co-monomer more suitable than IPDI to increase the relative amount of urethane bonds in respect to urea bonds. Moreover using DIE as co-monomer homogeneous distribution and noticeable penetration depth of the synthesized polymer inside the stone is achieved. The consolidating treatments were proved to prevent the complete obstruction of the stone porosity, this result being confirmed by the morphological analysis and the permeability to water vapour measurements. A good protective effect of urethane-urea copolymers was also evidenced by the strong decrease of the water capillary absorption in the treated samples. Finally the decrease of disaggregation and pulverisation phenomena under applied stresses were assessed through abrasion tests. It was shown that comparatively higher consolidating and protective properties are achieved by using DIE as isocyanate co-monomer in the reaction system.

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