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Preparation and Characterization of Polyesterurethane Metallopolymers Containing Transition Metal Ions

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Summary: Several series of metallopolymers (MP) were synthesized from a MDI-based polyesterurethane and various transition metal ion species, namely, copper(II), manganese(II), cobalt(II), iron(III) and chromium(III). Each series of MP were prepared by using different initial molar ratios urethane groups/metal ions (U/M). MP were characterized in comparison with the parent polyurethane (PU) by atomic absorption spectrometry (AAS), UV-vis absorption spectroscopy, FT-IR spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and tensile testing. The transition metal ions form coordination complexes with polyurethane functional groups, the intermolecular complexation resulting in the crosslinking of polymer chains. As a consequence, modifications take place in the original structure of PU, e.g. hydrogen bonding and crystallinity of the hard-segment domains. MP compared with PU present differences in viscoelastic and mechanical behaviors, which generally indicate the reinforcing effect of metal ions on the polyurethane matrix, as well in thermal stability. It was revealed that each transition metal ion has specific effects on the structure and properties of PU. The implications and mechanisms behind these observations are discussed.

Keywords: FT-IR; metal-polymer complexes; polyurethane; thermal properties; UV-vis spectroscopy

Introduction

The investigation of the synthetic polymer-metal ions systems gained increasing importance in the last decades. The study of the interactions occurring in these systems can provide valuable information on the capability of polymers to retain metal ions and the influence of the latter (as additives, contaminants or catalyst residues) on the synthesis and processing of the former.[1–3] By selecting the appropriate reactants and synthesis conditions, metallopolymers suitable for a variety of potential applications may be tailored.[4,5] In our papers, the interactions taking place in systems consisting of various metal ion species and different types of polymers have been investigated.[6–21] Polyurethanes are an important class of industrial polymeric materials, therefore it is of great importance to study the manner in which their structure and properties are affected by metal ions; meantime, polyurethane-based MP may be used as polymeric electrolytes, actuators, transducers etc.[22] In the present work, several series of MP were prepared from a polyesterurethane and various transition metal ions and characterized in comparison with the parent polymer by AAS, UV-vis absorption spectroscopy, FT-IR spectroscopy, DSC, DMA, TGA and tensile testing.

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Experimental Part

Synthesis

MP, denoted as MP-Cu, MP-Mn, MP-Co, MP-Fe and MP-Cr, were synthesized from a linear segmented polyurethane (having 3.26×10^{-3} mol · g^{-1} urethane group concentration) and copper(II), manganese(II), cobalt(II), iron(III) and chromium(III) ions, respectively, as chlorides (details on synthesis and sample preparation have been presented previously).[14] The polymer chains contain alternating soft segments consisting of poly(ethylene-co-diethylene adipate)diol (PEDA) and hard segments formed of 4,4′-diphenylmethane diisocyanate (MDI) and ethylene glycol (EG) as chain extender. For each metal ion species, a series of MP were prepared by using different initial molar ratios U/M ranging from 180:1 to 12:1 (Table 1). In the same conditions as MP, a reference sample (PU) was prepared from the polyesterurethane without metal salt. MP and PU were obtained in the form of films of about 80 μm thickness by casting from N,N′-dimethylformamide (DMF) solutions. By contrast to the colorless PU, MP exhibit specific colors showing that complexation occurs between metal ions and polyurethane functional groups; the lower the initial molar ratio U/M, the more intense the color.[9] MP are partially crosslinked materials as they are less soluble in DMF than PU due probably to the intermolecular complexation of metallic ions. MP exhibit, by contrast to PU, good adhesion to glass and silicone paper substrates.

Analyses

The metal content was determined by AAS using a Perkin Elmer AA800 spectrometer. The UV-vis absorption spectra were acquired in the wavelength range 280–770 nm at ambient temperature on a SPECORD M42-Carl Zeiss Jena spectrophotometer at a resolution of 2 cm^{-1}. The FT-IR spectra were recorded by attenuated total reflectance (ATR) method in the wavenumber range 400–4000 cm^{-1} using a Brucker VERTEX 7-Specac Golden Gate spectrophotometer at a resolution

Table 1.
Molar ratios urethane groups/metallic ions (U/M) in the initial systems and MP.

Initial system		MP		
Composition	Molar ratio U/M	Symbol	Molar ratio U/M	Color
PU/$CuCl_2 \cdot 2H_2O$	180:1	1Cu	213.3:1	greenish yellow-brown
	90:1	2Cu	137.8:1	
	60:1	3Cu	89.7:1	
	45:1	4Cu	85.9:1	
	36:1	5Cu	71.1:1	
	18:1	6Cu	66.5:1	
	12:1	7Cu	50.1:1	
PU/$MnCl_2 \cdot 4H_2O$	180.2:1	1Mn	358.1:1	brownish yellow
	60.1:1	2Mn	81.1:1	
	36:1	3Mn	44.4:1	
	12:1	4Mn	13.8:1	
PU/$CoCl_2 \cdot 6H_2O$	180.2:1	1Co	480.3:1	light greenish-blue
	60.1:1	2Co	100.8:1	
	36:1	3Co	76.5:1	
	12:1	4Co	19.8:1	
PU/$FeCl_3 \cdot 6H_2O$	180.2:1	1Fe	303.2:1	reddish brown
	60.1:1	2Fe	67.0:1	
	36:1	3Fe	35.9:1	
	12:1	4Fe	21.7:1	
PU/$CrCl_3 \cdot 6H_2O$	180.2:1	1Cr	188.0:1	yellowish green
	60.1:1	2Cr	73.3:1	
	36:1	3Cr	37.2:1	
	12:1	4Cr	18.6:1	

of 2 cm^{-1}. The DSC analyses were conducted on a Mettler DSC 12E instrument; samples of about 2 mg were heated at a rate of 20 °C min^{-1} from ambient temperature to 360 °C. The DMA measurements were per-formed at a heating rate of 3 °C min^{-1} from −120 to 200 °C using a TA Instruments DMA 983 apparatus; the dimensions of the multilayer samples were 50 × 30× about 0.8 mm. The TGA measurements were performed on a TGA V5.1A DuPont 2000 thermoanalyzer under dynamic nitrogen atmosphere at a heating rate of 9 °C min^{-1} from ambient temperature to 950 °C, the sample mass being 10 mg. The tensile tests were conducted at a crosshead speed of 5 mm · min^{-1} on a computer-controlled tensile tester; the dimensions of the dumbbell-shaped specimens were 45 × 7 mm with gauge dimensions 14 × 4 mm.

Results and Discussion

Atomic Absorption Spectrometry

In general, MP contain lower amounts of metal ions than those added in the corresponding initial systems and, accordingly, their molar ratios U/M are higher than the initial ones (Table 1 and Figure 1).[9] Meantime, in all MP series, the metal content increases with increasing amount of initially available ions. Of the maximum metal contents in the different series, that of MP-Mn is the highest, whereas that of MP-Cu is the lowest (1.26 and 0.41%, respectively). As suggested by the shapes of the MP metal content versus initial metal concentration plots, it seems that, under the specific preparation conditions, the contents of manganese, cobalt, iron and chromium ions of MP could further be increased by increasing the corresponding initial concentrations; by contrast, a saturation phenomenon tends to occur for copper ions, i.e. the polyurethane maximum capability of binding these ions is approached.[6,15,20,21]

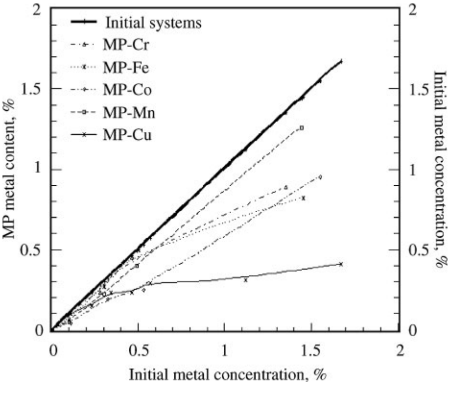

Figure 1.
Dependence of MP metal content on the metal concentration in the initial systems.

UV-vis Absorption Spectroscopy

The absorption capacities of MP are higher than that corresponding to PU over the entire wavelength range. By contrast to PU, which exhibits no absorption band between 300 and 770 nm, MP generally present three partially overlapped bands with absorption maxima decreasing with increasing wavelength. The intense band appearing as a shoulder in the near ultraviolet region, centered around 310 nm, may be attributed to a charge transfer transition. In the visible region, the two bands with absorption maxima located around 400 and 560 nm (670 nm only for MP-Co), the former being much more intense than the latter, are assignable to d–d transitions; in the same series of MP, the larger the metal content, the higher the absorbance (A_n) at the same wavelength, indicating increasing complexation (Figure 2). Among MP series, MP-Fe have the highest absorption capacity in the visible region (Figure 2d), whereas MP-Co the lowest (Figure 2c). Since the polyurethane possesses several types of sites with complexing ability towards transition metal ions, each MP presumably consists of a mixture of complexes, in which a certain complex structure prevails. A series of MP show resembling profiles of the absorption spectra, which suggests that the predominant structures are essentially the same, irrespective of metal content.

Fourier Transform Infrared Spectroscopy

Segmented polyesterurethanes generally exhibit microphase-separated morphology, consisting of hard-segment crystalline domains (containing a spatial system of hydrogen bonds) dispersed in a soft-segment (polyester) amorphous phase.[23] The PU spectrum exhibits the characteristic bands of MDI-based polyesterurethanes (Figure 3).[24,25] In the N–H stretching region, the single band centered at 3323 cm^{-1} may be assigned to the N–H groups associated through hydrogen bonds with urethane carbonyl groups.[26–28] In the carbonyl stretching region, the two intense bands at 1705 and 1727 cm^{-1} could be attributed to hydrogen bonded and free carbonyl groups, respectively, belonging to urethane groups in the hard-segment domains (amide I) and ester groups in the soft-segment phase, respectively; the hydrogen bonding index (HBI) may serve as a measure of the extent to which carbonyl groups participate in hydrogen bonding.[29] In comparison with PU spectrum, MP spectra show significant modifications,

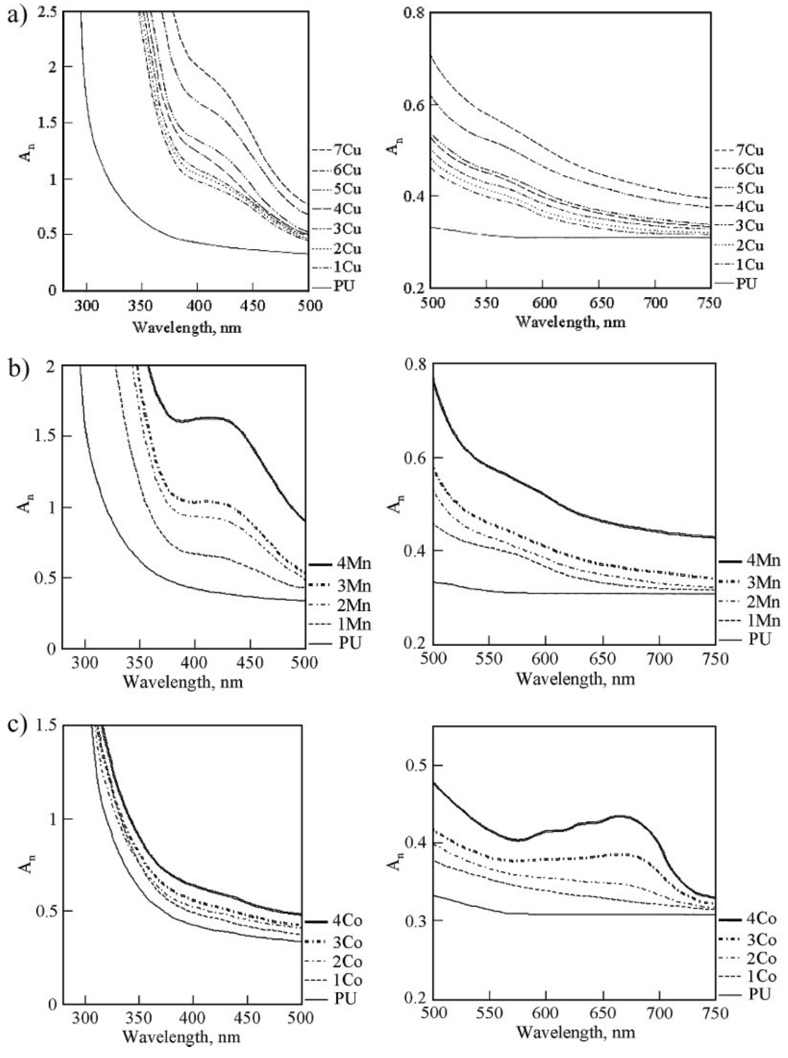

Figure 2.
UV-vis absorption spectra of PU and MP: a) MP-Cu; b) MP-Mn; c) MP-Co; d) MP-Fe; e) MP-Cr.

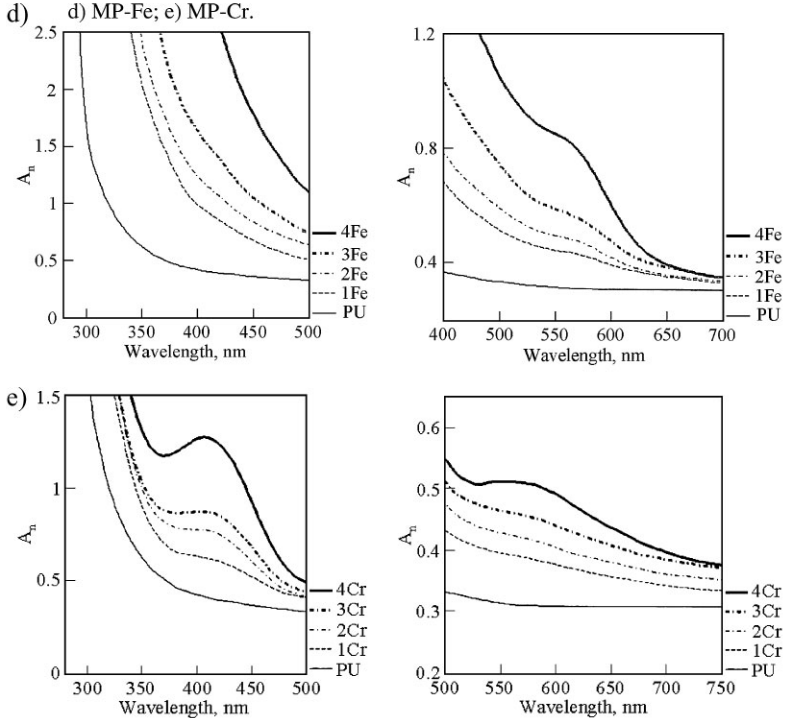

Figure 2.
(Continued).

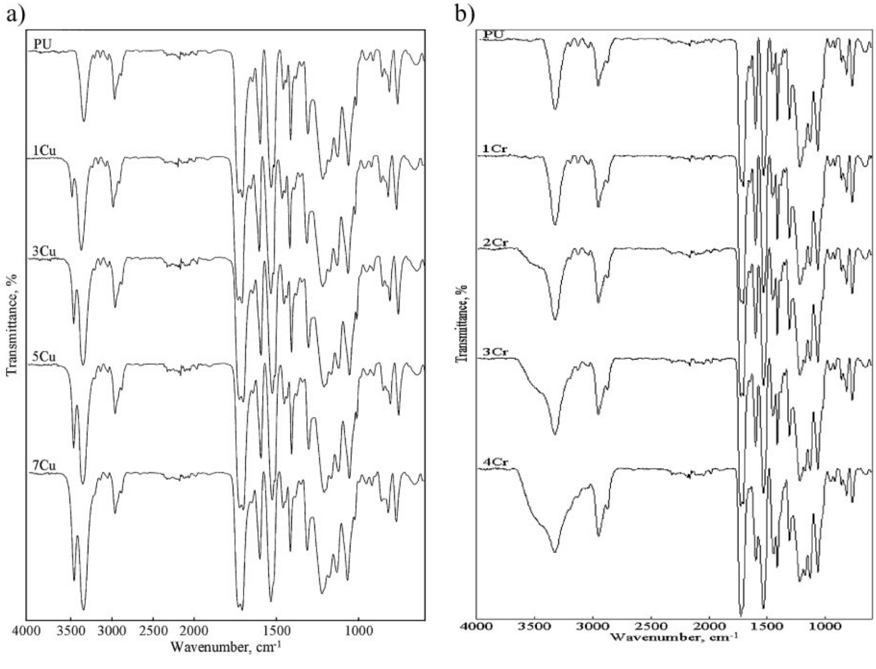

Figure 3.
FT-IR spectra of PU and MP: a) MP-Cu; b) MP-Cr.

e.g. those taking place in the N–H stretching region. For example, MP-Cu (Figure 3a) show two sharp, partly overlapped bands at about 3339 and 3448 cm^{-1}, which may be ascribed as follows: the former – to complexed and hydrogen bonded N–H groups, whereas the latter – to free N–H groups; their increase in intensity occurring with increasing copper content supports the assumption that the number of both complexed and free groups increases, whereas that of hydrogen bonded groups accordingly decreases.[6] The absorption coefficients of bonded and nonbonded N–H bands are usually different, preventing quantitative estimations.[26] The carbonyl and ether bands are generally unaltered for MP-Cu compared with PU, which could indicate that the oxygen atoms do not participate in complex formation. Besides the changes in the N–H stretching region, other important modifications may be shown by MP spectra. For MP-Cr (Figure 3b), for example, as chromium content increases, the band at 1457 cm^{-1} (presumably with an amide II contribution consisting mainly of N–H bending vibrations) displays a significant intensity increase due probably to the complexation of urethane nitrogen atoms with chromium ions, whereas HBI gradually decreases, which seems to be consistent with the breakage of the initial hydrogen bonding evidenced by N–H stretching region.[20] The FT-IR results reveal that, on one hand, the functional groups of the polyesterurethane provide active sites capable to form complexes with the transition metal ions and, on the other hand, the complexation produces the disturbance of the original hydrogen bonding of the hard-segment domains.

Based on the experimental results and literature data, the predominant structures of the complexes may be assumed.[6,20,21]

Differential Scanning Calorimetry

In all DSC experiments, the first heating scan was considered, as the second one would be affected by the thermal degradation of the hard segments. All studied samples have the same thermal history, since they were subjected to identical thermal treatments during preparation. The DSC analyses reveal the influence exerted by transition metal ions on the melting transition and crystallinity inherent to PU.[6,15,20,21] The DSC scans (Figure 4) show, over the 300 to 350 °C temperature range, endotherms resulting from the thermal disruption of the crystalline hard-segment domains. By contrast to PU, which exhibits a single melting endotherm, whose maximum is located at 328 °C, MP may present multiple melting endotherms, which could be explained by the coexistence in the hard-segment domains of crystal populations with distinct sizes, forms or degrees of perfection. The shifting of the melting endotherms of MP towards lower temperatures taking place with increasing metal content suggests that the presence of metal ions induces a decrease of order within the hard-segment domains; the most pronounced differences are exhibited by MP-Fe. For MP-Mn, MP-Co and MP-Fe with higher metal contents, the melting endotherm is partially overlapped by a broad endotherm occurring at higher temperatures, which is presumably caused by the onset of the thermal decomposition process; this assumption is supported by the favoring effect of manganese, cobalt and iron ions on the first two steps of thermal decomposition revealed by DTG curves presented in Thermogravimetric Analysis section. The crystallinity degree of PU is affected to different extents by various ion species, copper ions inducing the most pronounced amorphization of the hard-segment domains. In a MP series, the crystallinity tends to decrease as metal content increases (for example, in MP-Cu with the highest copper content the crystallinity is almost completely suppressed), whereas the extent of metal complexation increases; this seems to indicate that the complexes formed by the metal ions with the functional groups of the hard segments are mostly amorphous, meaning that the melting of the crystalline hard-segment domains of the pure polymer takes place

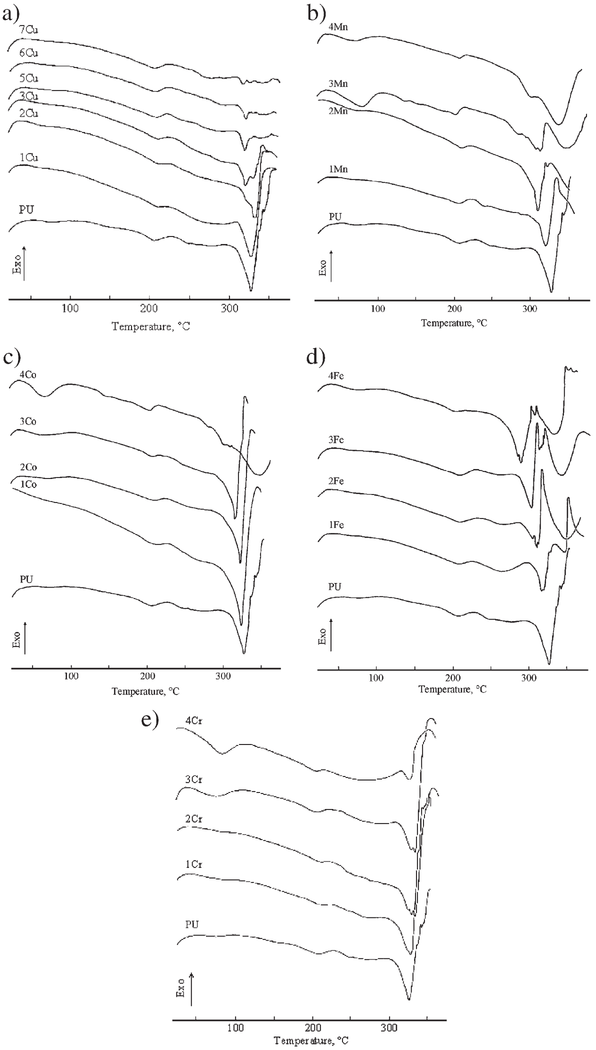

Figure 4.
DSC spectra of PU and MP: a) MP-Cu; b) MP-Mn; c) MP-Co; d) MP-Fe; e) MP-Cr.

actually. The capability of urethane segments to achieve the crystalline order may be diminished due to the crosslinking caused by the intermolecular complexation of transition metal ions, which restricts polymer chain motions for proper orientation. In PU, the minor endotherm occurring in the range of about 70–80 °C may be attributed to the dissociation of urethane-soft segment hydrogen bonding; its low intensity suggests a good phase separation with a rather small number of hydrogen bonds of this type.[30,31] Such hydrogen bonds may involve the individual hard segments dispersed in the soft-segment phase and those located at the borders of the hard-segment domains. MP (excepting MP-Cu) with higher metal contents exhibit an increase in endotherm intensity, which could be explained by an increase of phase mixing (i.e. the degree of hard segment mixing with the soft-segment phase), possibly caused by the decrease of the extent of association between the hard segments by hydrogen bonding, occurring concomitantly with the complexation.[32]

Dynamic Mechanical Analysis

The curves representing the temperature (*T*) dependence of loss tangent (tan δ) and storage modulus (*E'*) for PU and MP were obtained.[6,20,21] For PU, the curve tan δ–*T* exhibits two peaks with maxima at 13 and −61 °C, labeled α and β, respectively (Figure 5). The main relaxation (peak α) is identifiable as the glass transition of the soft segments; the temperature at the maximum tan δ is the glass transition temperature (T_{gs}).[33] The mobility of the soft segments is restricted by the phase separated hard segments (anchoring effect), as well as by the hydrogen bonds formed within the soft-segment phase (involving the isolated hard segments) and/or at the borders of the hard-segment domains. Peak β is attributed to a secondary relaxation taking place in the soft-segment phase caused by local motions of consecutive methylene and/or ester and/or ether groups or breaking of hydrogen bonds occurring between hard and soft segments.[34] For MP as compared with PU, the T_{gs} values increase and the temperature ranges of the glass transition broaden (Figure 5). Generally, the shape of tan δ–*T* curve for MP with the maximum metal content is significantly different from that of PU; peak α has larger area and increased asymmetry. It appears that the soft-segment phase is sensitive to the presence of transition metal ions in the polyurethane matrix. The changes in the glass transition of the soft segments could be induced by their crosslinking through metal ions and by the anchoring effect exerted on them by the metal ions-containing hard domains.[35] The higher T_{gs} values for MP-Cu, for example, compared with that of PU could be explained in terms of the limitations in soft segment mobility produced by the

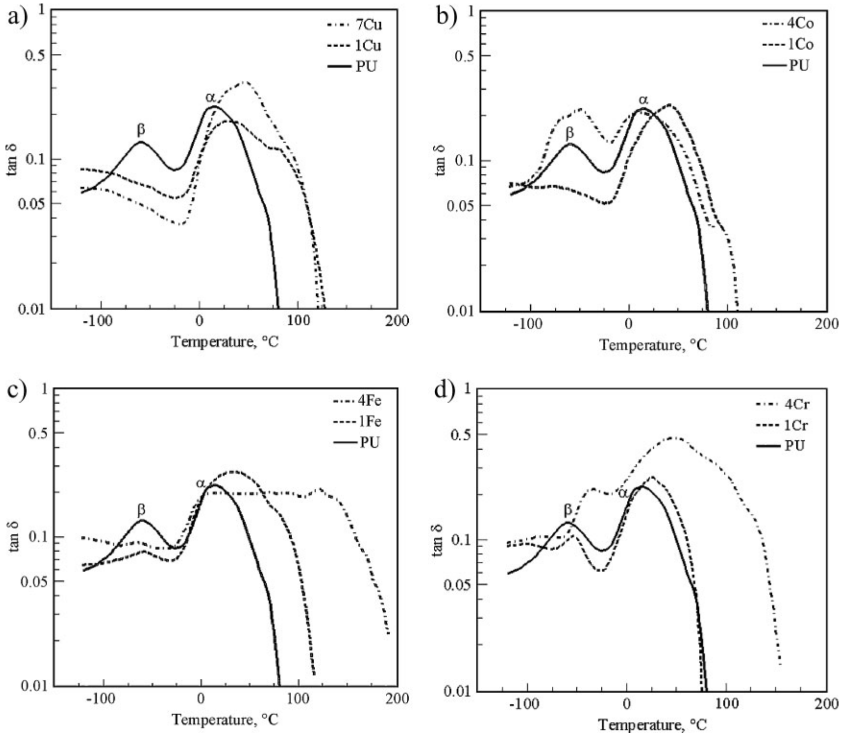

Figure 5.
Dependence on temperature of loss tangent (tan δ) for PU and MP: a) MP-Cu; b) MP-Co; c) MP-Fe; d) MP-Cr.

coordination crosslinking occurring within the hard-segment domains (Figure 5a); the increase in T_{gs} with increasing metal content seems to reveal a direct correlation between the transition upward shift and the crosslinking increase.[6] The modifications taking place in the secondary relaxation (peak β) could indicate changes in the hydrogen bonding occurring between hard and soft segments. MP exhibits higher values of *E'* than that corresponding to PU, revealing the reinforcing effect of the transition metal ions (especially copper and cobalt) on the polyurethane matrix. In MP-Cu, MP-Co and MP-Fe series, MP with the minimum metal content shows higher *E'* values than that with the maximum metal content, suggesting that the lower amount is comparatively more efficient in increasing chain stiffness; this behavior could not be accounted for only by the crosslinking level, but presumably also by hydrogen bonding and morphology.

Thermogravimetric Analysis

The DTG curves illustrating the dependence on temperature of derivative weight loss are considered for PU and MP (Figure 6).[9,12–14] The thermal degradation of PU consists of two consecutive stages taking place in the temperature ranges of about 200–515 and 515–730 °C, comprising five steps with the maximum volatilization rates occurring around 270, 310, 360, 400 and 610 °C. The decomposition steps may be tentatively assigned to the degradation of polyurethane constituents (step I – EG, step II – MDI, steps III and IV – PEDA) and isocyanurate-containing products formed via secondary reactions of MDI (step V). The comparative study of the modifications induced by the five transition metal ions in the non-oxidative degradation of the polyurethane revealed that each one of them affects, in a complex and distinct way, the process. The presence of all metal ions influences both decomposition stages, but the effects of a certain ion species on the decomposition steps are different in type (i.e. catalytic or inhibiting) and/or extent. It was shown, by comparing several thermal characteristics, such as maximum rates of mass loss, temperatures and temperature ranges, that every ion species has a specific influence on the polyurethane thermal degradation. Manganese, cobalt and iron ions favor, to different extents, the degradation of the polyurethane. Chromium and copper ions, in different degrees, reduce the initial thermal stability of polyurethane and catalyze the final stage of its degradation, but, by contrast, enhance the thermal stability of its intermediate decomposition products. In general, the effect of the transition metal ions on polyurethane thermal degradation is increasingly significant as their amount is higher. All metal ions induce changes in the decomposition mechanism of the polyurethane.

Tensile Testing

The mechanical properties of segmented polyurethanes are mainly accredited to the pseudo-crosslinking effect caused by the hard-segment aggregation, the resulting hard-segment domains functioning as reinforcing fillers for the soft-segment amorphous phase.[36] The stress-strain curve of PU is typical for elastomers (Figure 7); the values of elongation at break and tensile breaking strength are about 560% and 36 MPa, respectively. The stress-strain curves of MP-Cu and MP-Mn, for example, are largely similar in shape with that of PU (Figure 7).[6] The stress values of MP and the corresponding one of PU are not very different below about 150–200% strain, indicating rather similar deformation mechanisms. Thereafter, the tensile strength values of MP are higher than that corresponding of PU, revealing the reinforcing role of copper and manganese ions on the polyurethane matrix. It may be assumed that the coordination crosslinking of the hard segments renders the hard-segment domains rigid, these orienting into the stretch direction as structurally intact units. The amorphous bundles of crosslinked hard segments restrict the ability of the soft segments to become highly oriented, thus limiting the amount of stress-induced crystallization in the soft-segment phase,

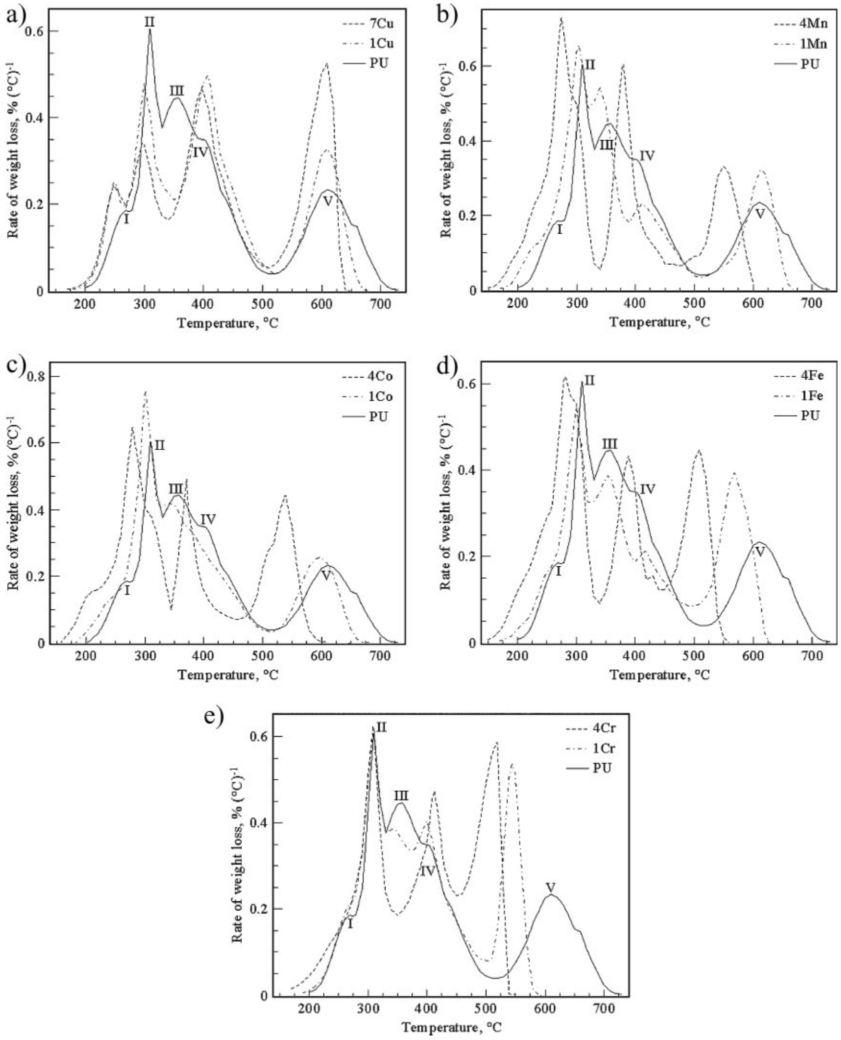

Figure 6.
DTG curves for the thermal decomposition of PU and MP: a) MP-Cu; b) MP-Mn; c) MP-Co; d) MP-Fe; e) MP-Cr.

whereas the remaining crystalline regions of the hard-segment domains are free to break away from the domains and orient independently into the stretch direction. The stress necessary to produce a certain strain tends to decrease with increasing metal content, although the reverse situation would be expected. This behavior suggests that the mechanical response of MP is the resultant of various interrelated phenomena concerning both the hard-segment domains (coordination crosslinking, hydrogen bonding and crystallization) and the soft-segment phase (stress-induced crystallization). For MP-Cu and MP-Mn compared with PU, the values of the elongation at break are lower, confirming that the incorporation of copper and manganese ions results in enhanced rigidity of the polyurethane matrix.

Conclusions

The MP synthesized from a segmented polyesterurethane and transition metal ions

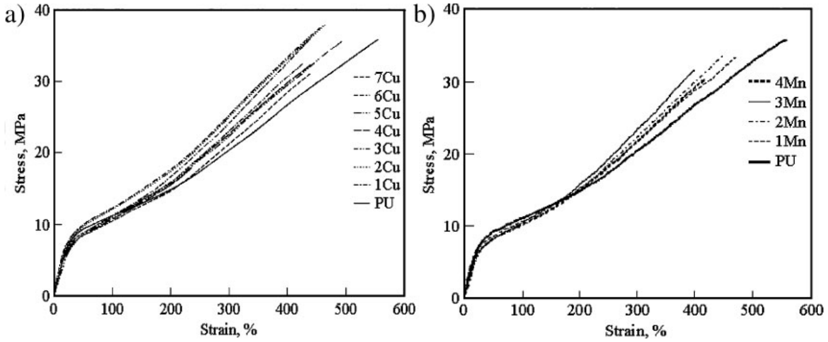

Figure 7.
Stress-strain curves of PU and MP: a) MP-Cu; b) MP-Mn.

as chlorides exhibit specific color properties, as well as better adhesion to glass and lower solubility in DMF as compared with PU. The metal content of MP, although tends to increase with increasing amount of metal ions used in their synthesis, is always smaller than this. As a consequence of the formation of coordination complexes between metal ions and the polyurethane functional groups, the hard-segment domains undergo the disturbance of the original hydrogen bonding and crystallinity. In comparison with PU, MP present changes in the viscoelastic and mechanical behaviors due to the decrease of chain mobility caused by coordination crosslinking; they exhibit higher values of the soft-segment glass transition and storage modulus, as well as enhanced tensile strength and lower elongation at break. For MP compared with PU, the initial thermal stability is lower and the final stage of thermal decomposition is catalyzed; the thermal stability of the intermediate decomposition products is enhanced or reduced depending on the ion species.

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