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Chemical modifications of functional polybutadienes and their derivatives

Part 1. Use of meta isopropenyl-α,α'-methyl benzyl isocyanate (TMI)

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Summary

The synthesis of a multi(α-methyl styrene) oligomer containing a polybutadienic chain was achieved from the condensation of hydroxytelechelic polybutadiene (HTPB) with meta isopropenyl-α,α'-methyl benzyl isocyanate (TMI). Then, formulations from modified HTPB with various acrylic reactive diluents containing lauryl acrylate and hexane-1,6-diol diacrylate (HDDA) were investigated and compared with classical polyurethanes. Various physical properties (viscosity, shore hardness and gel time) and thermal properties (glass transition and degradation temperatures) were studied and discussed.

Introduction

Polybutadienes are very interesting polymers because of their very low Tg (-80°C) and lead to materials with good softness properties. Beside the sulphur cured elastomers, many other polymers have been prepared starting from liquid telechelic oligomers such as hydroxy telechelic polybutadienes (HTPB commercialized, for example, by the Elf-Atochem company) and carboxy telechelic polybutadienes (CTPB from Goodrich). From HTPB, polyurethane networks have been prepared, and they are involved for example in solid propellants (1) or in the protection of electronic devices.

However, the use of diisocyanates induce various environmental problems either in the synthesis (toxicity of the diisocyanates) or in the recycling (toxicity of aromatic diamine and gas released by burning). Consequently, many researchers have tried to modify these compounds and introduced various groups different from the hydroxyl function. Hence, numerous industrials prefer using multifunctional polybutadienes in UV curing to avoid solvents and to obtain a rapid curing. For this purpose above, two kinds of modification can be performed, either in the chain or at the both ends of the polybutadienic chain.

Concerning the first one, Chhim (2), Le Xuan and Decker (3) and Burfield et al. (4) have first developed the epoxidation of some double bonds and then esterified the epoxide groups by acrylic acid.

In the same way, Derouet et al. (5) introduced cinnamic moieties after reaction of the polybutadiene with maleic anhydride.

As for us (6), we have modified the double bonds of carboxy telechelic polybutadienes by mercaptoacetic acid and then the use of glycidyl methacrylate led to polymethacrylic oligomers.

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Regarding the modification of the end groups, pioneered works were developed by Pinazzi et al. (7) who reacted HTPB with methacryloyl chloride and these products were further used by Kimura and Yamakawa (8) for coatings of optical fibbers; they were compared to siliconated homologues. Another method to obtain the same telechelic methacrylated product dealt with the transesterification of methyl methacrylate with HTPB (9).

However, the most used method to introduce acrylic moieties at both ends of HTPB concerns the use of diisocyanates, hydroxyethyl acrylate (HEA) and HTPB. They have been introduced either directly (10) or in two steps by Tyagly et al. (11) while Coudray et al. (12) preferred using the reverse process modifying HTPB by the adduct of the mixture of HEA and diisocyanate. These last authors and a Korean team (13) investigated the kinetics and the properties of polymers obtained from telechelic acrylated products and various acrylic diluents. In addition, the structure of these networks were compared with polyurethane homologues. However, Pascault's team (14) reported that the multiacrylated polybutadienes via diisocyanate often contain microgels, and that high viscosities of these prepolymers were noted because polycondensation reactions occured in the course of the syntheses.

The objective of this work concerns the synthesis of multifunctional polybutadienes obtained with meta isopropenyl-α,α'-methyl benzyl isocyanate (TMI). This polybutadiene contains urethane links and unsaturations (styrenic type) and appears very reactive (in radical polymerization) according to the Alfrey and Price parameters (Q = 1.30 and e = -1.06) (15). In this area, the only work was pointed out by Stretton et al. (16) who prepared TMI terminated polybutadienes. They briefly studied the homopolymerization of this compound for telecommunication applications (e.g., rerentrable polymers). However, it was worth improving the characterization of these oligomers and studying their ability in copolymerization with various reactive diluents, which is the objective of this paper.

Results and discussion

Synthesis and characterization of an unsaturated polybutadiene (STPB)

The reaction (HTPB and TMI) was performed in bulk at 50°C (nitrogen atmosphere) in the presence of dibutyl tin dilaurate (DBTDL) catalyst, as follows :

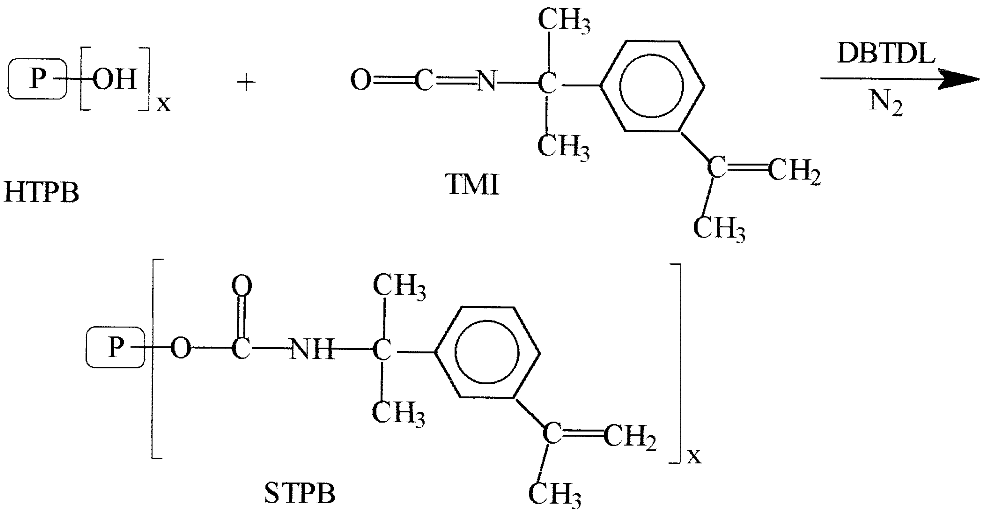
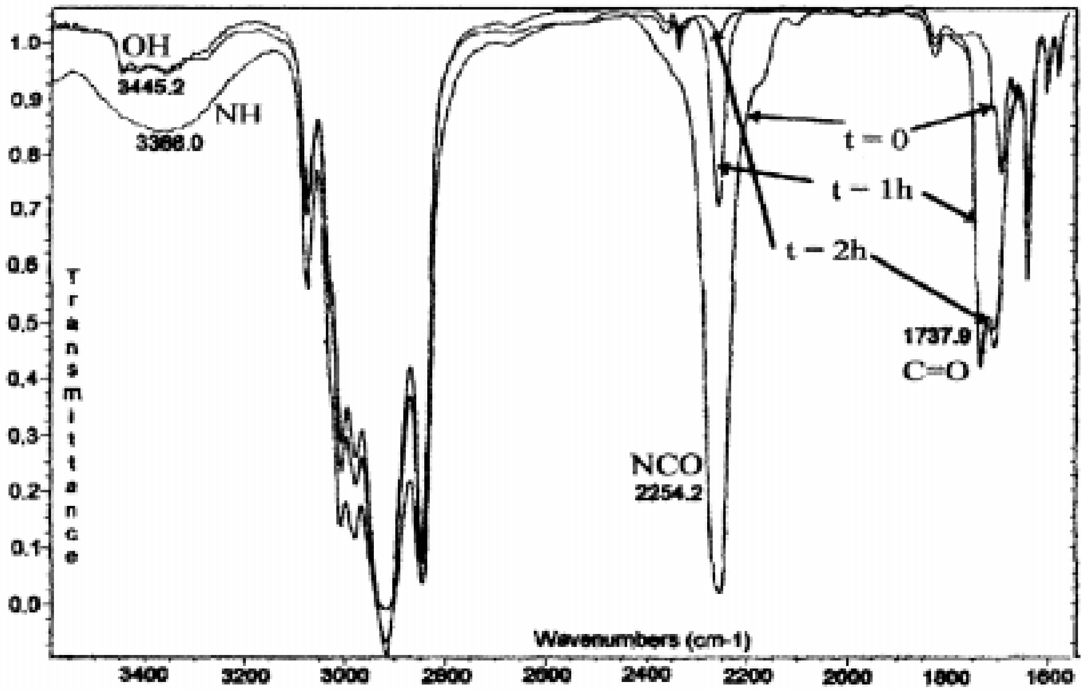


Figure 1 : Evolution of FTIR spectra of mixture of HTPB and TMI versus time

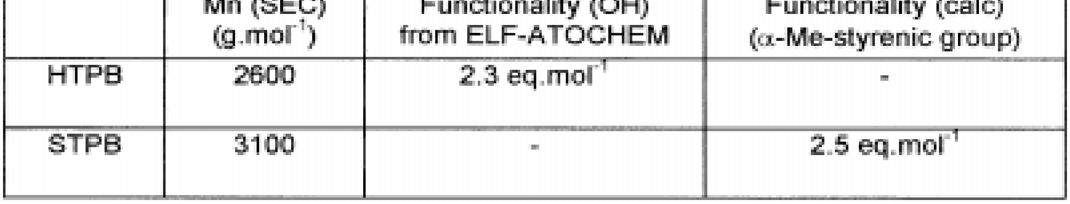


The reaction was monitored by FTIR spectroscopy by the decrease of NCO group at 2257 cm^{-1}. Figure 1 represents the evolution of that band versus time for a reaction with a slight excess of TMI (5%) about hydroxylated prepolymers. The reaction was stopped as soon as the absence of the NCO band was noted.

In the same way, ^{1}H NMR spectroscopy was used to monitor the reaction. Interestingly, the^{1}H-NMR spectrum (Figure 2) of the TMI shows the presence of two signals centred at 7.4 and 7.6 ppm assigned to aromatic protons and at 2.2 ppm for the methyl of α-Me styrene group. Styrenic unsaturation is represented by two signals centred at 5.2 and 5.4 ppm but they are overlapping with ethylenic protons of HTPB. The ^{1}H NMR spectra of the mixture of Poly BD R45HT® with TMI at t=0 and after reaction (at t=2h) exhibits different types of protons and the chemical shifts are well-shown in Figure 2. However, both signals centred at 3.5 and 4.1 ppm are assigned to the methylene groups adjacent to the hydroxy function (t = 0). After 2 hour-reaction, was noted the shift of 0.5 ppm of these two peaks to 4.0 and 4.5 ppm that confirms the complete formation of urethane bond.

The increasing of molecular weights (MW) from HTPB to STPB was monitored by size exclusion chromatography (SEC) using monodispersed polybutadienes as standards. Hence, in the case of Poly BD R45HT®, an increasing molecular weight was noted after reaction with TMI (Table 1).

Table 1 : Molecular weights and functionality of HTPB® and STPB.



	Mn (SEC) (g.mol^{-1})	Functionality (OH) from ELF-ATOCHEM	Functionality (calc) (α-Me-styrenic group)
HTPB	2600	2.3 eq.mol^{-1}	-
STPB	3100	-	2.5 eq.mol^{-1}

Indeed, the difference of both molecular weights corresponds to the product of the HTPB functionality (Fx) with the molecular weight of TMI, as shown in the following formulae :

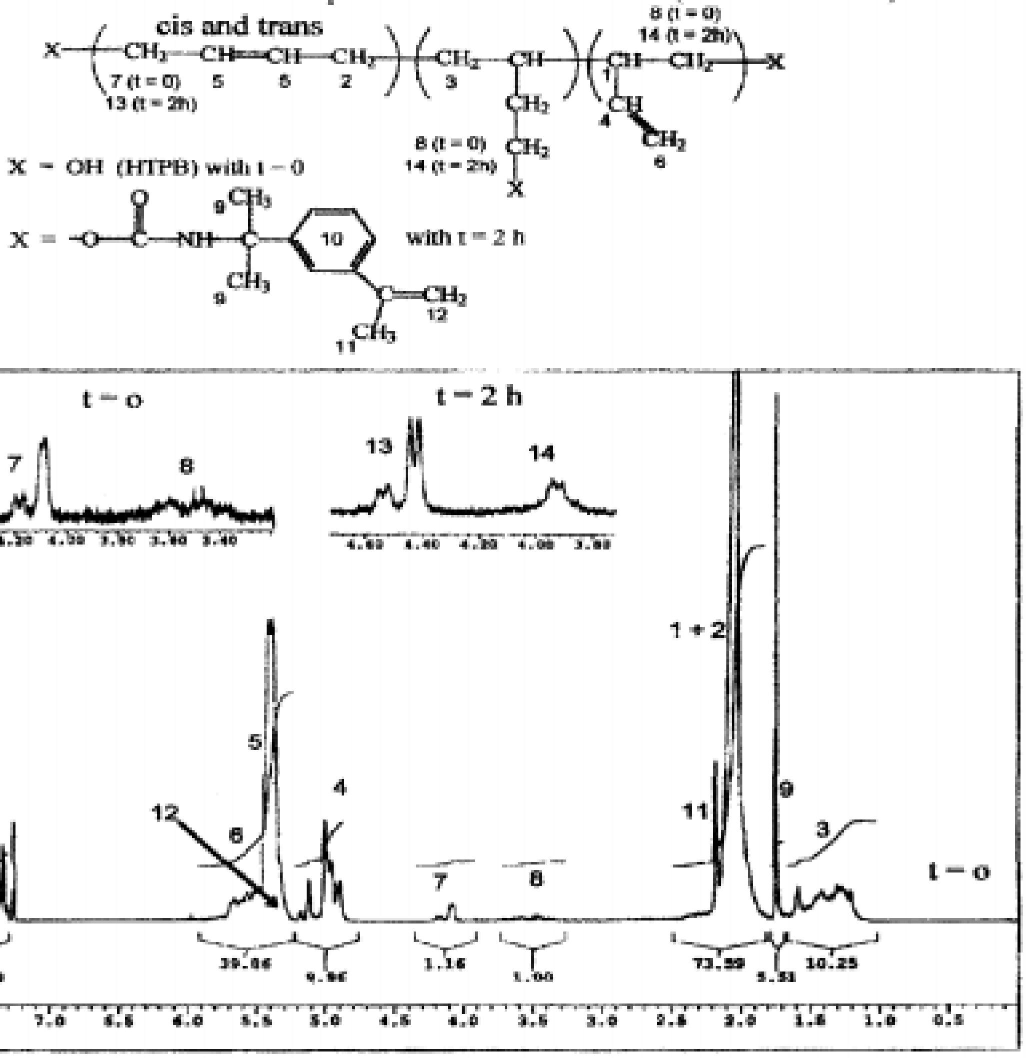
$$Mn_2 - Mn_1 = F_x {}^{*} M_{TMI}$$

where F_x, Mn_1, Mn_2 and M_{TMI} represent the styrenic functionality, the molecular weight of HTPB, the molecular weight of STPB and the molecular weight of TMI, respectively. These results showed the total conversion of hydroxyl groups and the presence of urethane links because HTPB and STPB has the same functionality (Table 1).

Processing of unsaturated polybutadiene and characterization of materials obtained

In the field of the protection of electric and electronic devices, polyurethanes are most often used and are regarded as references for our study. It was interesting to elaborate an acrylic system to improve properties and processing and they were compared to classical polyurethanes. Hence, the copolymerization with an acrylic reactive diluent in the presence of a peroxide initiator coupled with a catalyst of radical polymerization was investigated.

Figure 2 : Evolution of ^{1}H NMR spectra of HTPB and TMI (t = 0 and t = 2h)



It is well-known that cobalt salts associated to a peroxide produce a redox system which increases the decomposition rate of the initiator.

Usually, the formulation of an acrylic crosslinked resin is composed of a mixture of a monoacrylate and a diacrylate. Concerning the first one, lauryl acrylate homopolymer leads to flexible materials which exhibit very low glass transition temperature (Tg = -65°C). Regarding the second monomer, hexane-1,6-diol diacrylate (HDDA) and triethylene glycol diacrylate are generally used but HDDA supplies a better thermal stability. Hence, we performed four formulations (Table 2) which contained STPB, HDDA and lauryl acrylate as reactive diluent. The elastomers obtained were compared to a common polyurethane based on HTPB and dicyanatohexane.

Table 2 : Weights (g) of reactants involved in various formulations.

Formulation	1	2	3	4	5
HTPB R45	30.0	-	-	-	-
Dicyanatohexane	2.1	-	-	-	-
STPB	-	3.0	30.0	30.0	30.0
Lauryl acrylate	-	6.0	6.0	6.0	6.0
Hexane-1,6-diol diacrylate (HDDA)	-	2.0	1.0	1.0	0
Cobalt Naphtenate	-	0.1	0.2	0.1	0.1
tBu-Peroxypivalate	-	0.5	0.5	0.5	0.5

The applications of PU resins were mainly those of potting resins for the protection of electronic devices. Three physical parameters had to be taken into account and gave rise for the processability : The resin viscosity before crosslinking, the gel time to obtain networks and the shore hardness after crosslinking.

Same investigations were performed on acrylic resins and compared to those obtained from PU resins. Then, thermal analyses from elastomers were assessed.

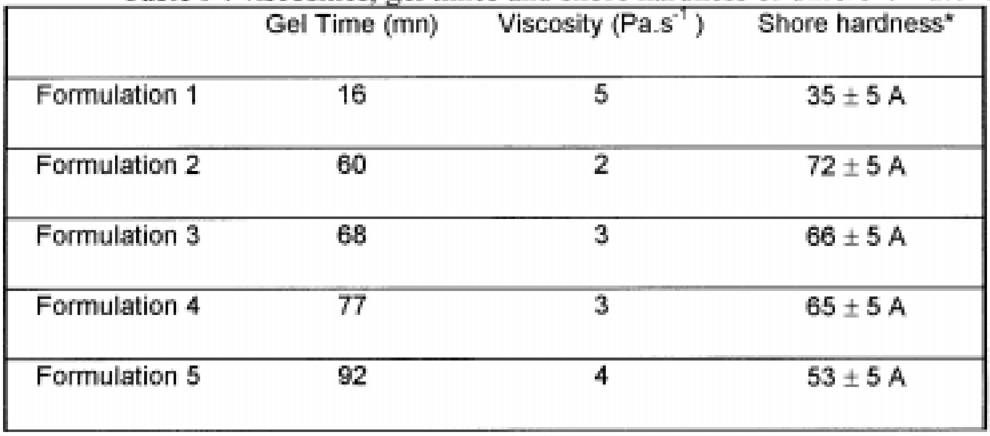
The viscosities and the gel times were carried out with the different resins at 30°C before hardening, by means of viscosimeter (TROMBOMAT supplied by PRODEMAT company). The results are listed in Table 3.

Interestingly, the viscosities of HTPB and STPB are 6 and 8 $Pa.s^{-1}$ at 30°C, respectively. The viscosity of PU resin is higher (5 $Pa.s^{-1}$) than those of the acrylic resins (2-4 $Pa.s^{-1}$) since these latters are diluted into fluid reactive monomers. In the case of PU resins, a plasticizer is usually introduced in order to lower their viscosities.

The gel time of PU resin is very short (< 20 mn) and depends directly upon both the contents of diisocyanate and DBTDL.

As for acrylic resin, various parameters can influence the gel time value. The first one depends upon the amount of cobalt salts added, as shown by the

Table 3 : viscosities, gel times and shore hardness of different materials



	Gel Time (mn)	Viscosity (Pa.s^{-1})	Shore hardness*
Formulation 1	16	5	35 ± 5 A
Formulation 2	60	2	72 ± 5 A
Formulation 3	68	3	66 ± 5 A
Formulation 4	77	3	65 ± 5 A
Formulation 5	92	4	53 ± 5 A

* Values expressed in A unit according to the NFT 51109 French standard.

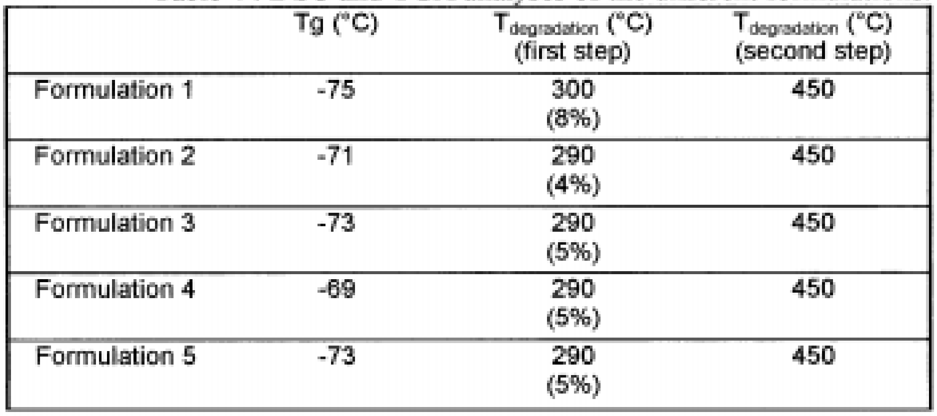
characteristics of formulations 3 and 4 (Table 3). The second one is influenced by the amount of diacrylate (HDDA) introduced since the compound acts as a curing agent; this is well-reported in formulations 2, 4 and 5. However, the gel time of acrylic resins is more difficult to monitor than that of the PU do, especially when gel times lower than 30 mn are searched.

Regarding the shore hardness according to the NFT 51109 French standard, acrylic resins lead to harder materials (50 to 70 A) than PU resins (35 A). From these unsaturated systems, highly crosslinked networks were obtained, in which the STPB chains act as bridges between poly(lauryl acrylate) chains (formulation 5). The density of the network is furthermore increased when a second difunctional (HDDA) is added that yields a further crosslinking. On the contrary, a plasticizer can be introduced in these acrylic resins to lower the hardness of the materials and to decrease the amount of acrylic monomers.

As for PU resins, the coupling of HTPB chains by diisocyanate only occured; the crosslinking comes from the high functionality of HTPB (2.3 eq.mol^{-1}) and that can explain the low hardness.

The results of thermal analyses, performed by Differential Scanning Calorimetry (DSC) and thermogravimetric analyses (TGA) are shown in Table 4.

Table 4 : DSC and TGA analyses of the different formulations.



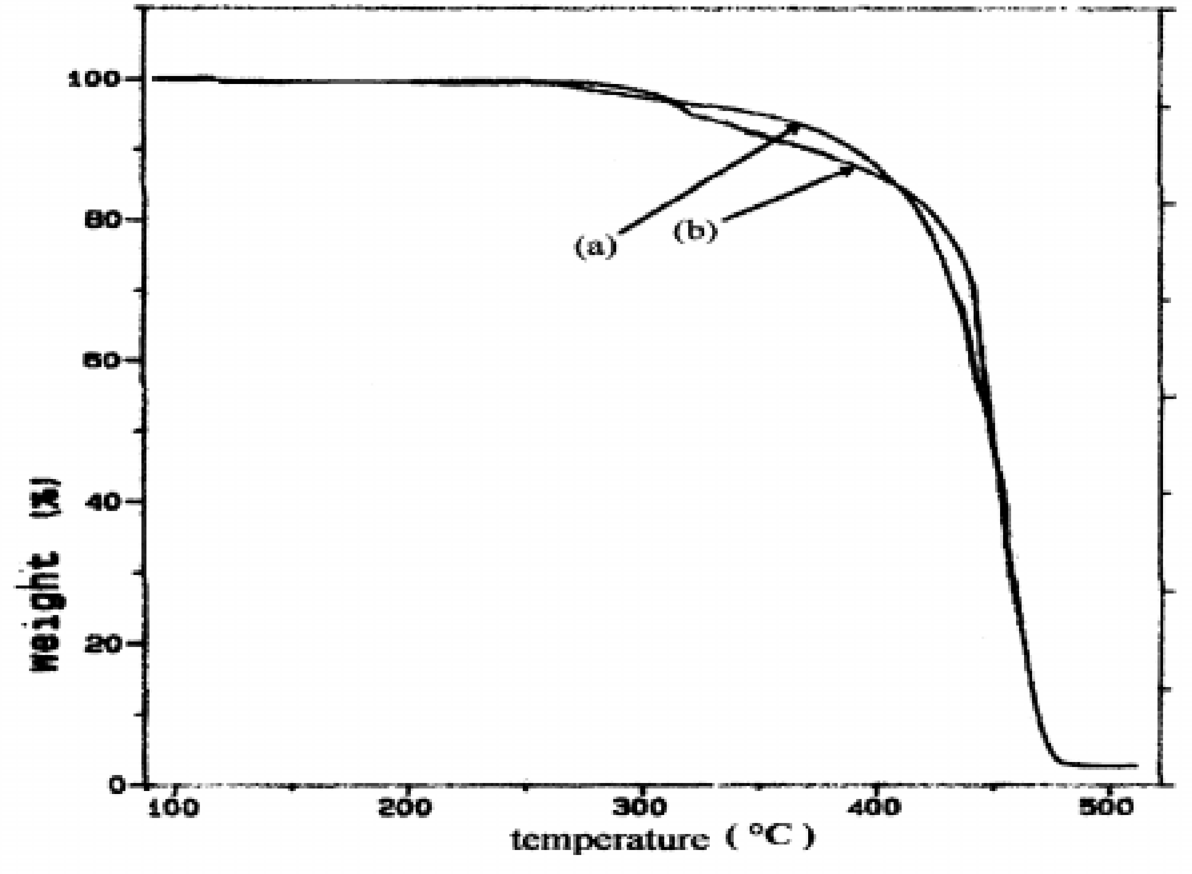
	Tg (°C)	$T_{degradation}$ (°C) (first step)	$T_{degradation}$ (°C) (second step)
Formulation 1	-75	300 (8%)	450
Formulation 2	-71	290 (4%)	450
Formulation 3	-73	290 (5%)	450
Formulation 4	-69	290 (5%)	450
Formulation 5	-73	290 (5%)	450

Interestingly, the glass transition temperature (Tg) was noted to remain almost constant (ca. -73°C) for the materials produced from all the formulations, in spite of the slight tendancy of an increase of the Tg in the case of unsaturated formulations. Moreover, none other Tg was observed for both PU resins (hard segment) and acrylic parts of our resins. Hence, the noted glass transition characterizes the polybutadiene phase. However, as homopolymer from lauryl acrylate exhibits a Tg close to that of HTPB, we cannot conclude to the existence of one or several soft phases. Scanning electron microscopy did not allow us to bring up clearness on the formation of a heterophased blend.

As for the thermal stability of the materials, the degradation temperatures were similar with mainly two weight losses. The first one, that occurs at about 300°C (Table 4), corresponds to the degradation of urethane links. But, in the case of unsaturated resins, the weight losses are reduced to 4%, whereas the ponderal fraction of TMI reached 10% in the resin because in the course of the degradation (300°C), (α-Me-styrene moieties remained linked to the acrylic chain. On the contrary, for polyurethane resins, the weight loss (8%) corresponds to the ponderal fraction of HDI introduced in the resin. The second degradation occurs in all cases at ca. 450°C and is attributed to the decomposition of polybutadienic chains as already shown (17).

However, for PU resin, the first degradation seems to occur slightly at higher temperature (Figure 3). This can be explained by the nature of the urethane link formed from HDI slightly more thermally stable than that produced from TMI. In contrast, the amplitude of these weight losses vary conversely. But it is assumed that the acrylic network remained unchanged at these temperatures (300°C) while for PU resins, the network was entirely decomposed.

Figure 3 : Thermograms of PU acrylate from formulation 2 (a) and classical PU from formulation 1 (b) (under N_2, heating rate : 5°C/mn)



To conclude, this study shows that the materials obtained from unsaturated polybutadienes coupled to reactive diluents totally differ from PU resin prepared from HTPB on both the mechanical and the thermal properties. Further work is under progress.

Acknowledgments

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