PII: S0032-3861(97)00355-8

Low molar mass polybutadiene made crosslinkable by the introduction of silane moieties via urethane linkage: 2. Crosslinking study

F. Schapman, J. P. Couvercelle and C. Bunel*
Laboratoire de Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Place E. Blondel, BP 08, 76131 Mont Saint-Aignan Cédex, France
*(Received 17 March 1997; revised 22 April 1997)*

In the present paper we discuss the crosslinking of polybutadiene bearing alkoxy silane functions (PBUnSi), where n is the number of silanes per chain ($n = 1.2, 2, 2.4$). Crosslinking was carried out at different temperatures, with and without a catalyst. The best experimental conditions correspond to 80°C, under moisture with dibutyl tin dilaurate as the catalyst in the ratio of [DBTL]/[Si] = 5×10^{-3}. The reaction was followed by the measure of swelling (Q) in toluene and mechanical parameters (storage modulus (E'), E' at rubbery plateau and tan δ). The low rate of modification, essentially at chain extremities, leads to the molar mass per crosslinked unit ($\overline{Mc}$) being practically constant and thus to a weak increase of T_g whatever the n value. Only a drop of damping efficiency is observed during the crosslinking process. © 1997 Elsevier Science Ltd.

(Keywords: polybutadiene; silane; crosslinking; swelling; mechanical properties)

INTRODUCTION

The use of compounds like alkoxy silanes in polymer chemistry has greatly increased over the last twenty years. The main objects are either conceiving new materials with specific properties or crosslinking of commercial polymers by moisture in order to improve their physical or mechanical properties. For example, grafting of vinyl triethoxy silane onto polyethylene[1-3] in the presence of dicumyl peroxyde leads to better dimensional stability at high temperature, improvement of solvents and strain resistance after crosslinking. This process was also applied to PVC with vinyl silane[4], amino silane[5] or mercapto silanes[6]. Other well-known α,ω-hydroxy terminated polymers were also used, especially polydimethylsiloxane (PDMS)[7-10], polyoxytetramethylene (POTM)[11-14], polyoxyethylene (POE)[15,16], and hydrogenated polybutadiene (H-HTPB)[10,17]. Concerning polybutadiene, which is the purpose of this paper, alkoxy silanes were grafted onto a polymer backbone by using hydrosilylation of vinyl double bonds[18] or by radical addition of mercapto silanes always on vinyl double bonds[19]. In this last case, crosslinking was followed by i.r. spectroscopy (disappearance of Si–O–C band at 1180 cm^{-1} and appearance of Si–O–Si band at 1080 cm^{-1}) without continuous examination of material properties. In this work, we followed crosslinking progress by using swelling measurements and mechanical properties from an α,ω-hydroxy terminated polybutadiene (HTPB; with a mean hydroxyl functionality $\bar{f}_{OH} = 2.4$) modified by isocyanato propyl triethoxysilane (IPTS) in various ratios. $\bar{f}_{OH} = 2.4$ for HTPB implies that the number of silane groups per chain (n) may vary in the range 0–2.4, depending on the amount of IPTS made to react. Hydroxyl and isocyanate functions

leads to a urethane linkage as depicted below:
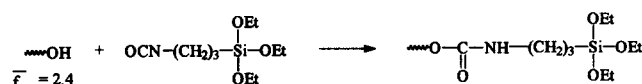
Three modified polymers, called PBUnSi ($n = 1.2, 2, 2.4$)[20], were used in this report.

EXPERIMENTAL

Materials

Polybutadiene (Poly Bd R45 HT®) was kindly supplied by Elf Atochem. Immobilisation of triethoxy silane moieties on polybutadiene by using isocyanato propyl triethoxy silane (Interchim) and dibutyl tin dilaurate (Aldrich) was described elsewhere[20].

Crosslinking conditions

Modified polybutadiene (PBUnSi), with and without a catalyst, was casted in a PTFE mould (2 mm depth) and placed into an oven at different temperatures. For crosslinking under moisture, a vessel containing water was introduced in the oven.

Measurements

Crosslinking was followed by two methods.

Swelling measurement. From polymer casting, samples ($8 \times 8 \times 2$ mm^3) were cut off during the crosslinking process and swollen in toluene for 24 h. Afterwards, samples were first weighed (m_s) then dried under vacuum for 24 h at room temperature and weighed again (m_d). Swelling (Q) is calculated as:

$$Q = \frac{m_s - m_d}{m_d}$$

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* To whom correspondence should be addressed. Tel: (33) 02 35 52 84 46; Fax: (33) 02 35 52 84 46.
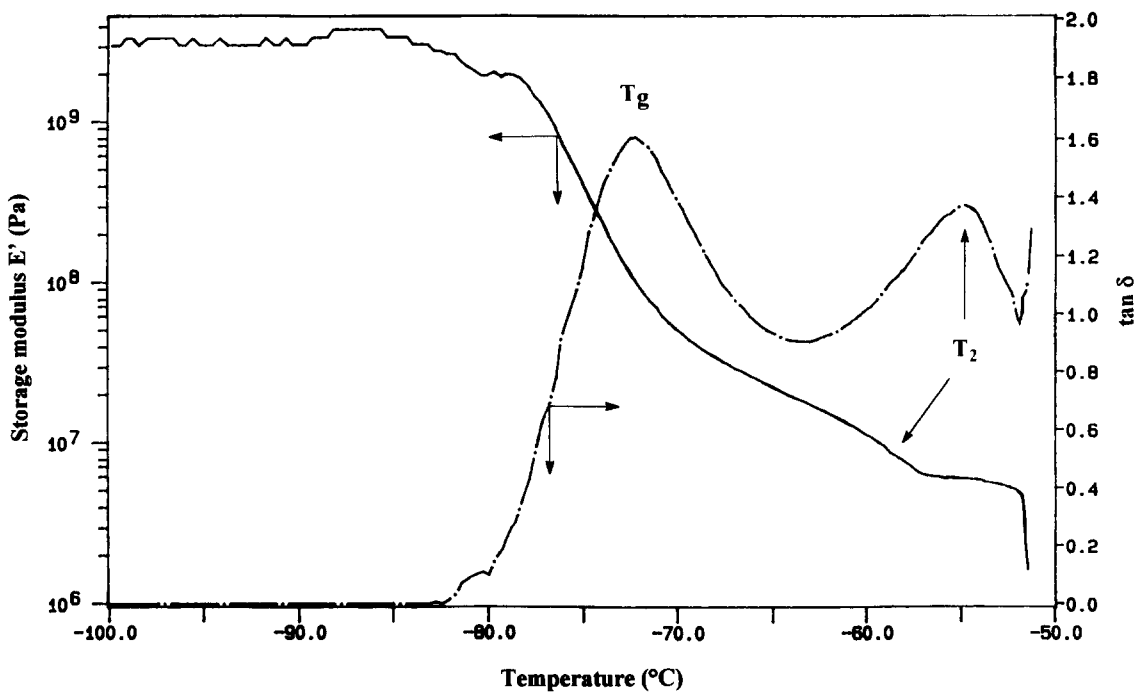
Figure 1 Storage modulus E' and tan δ versus temperature for initial HTPB

Mechanical properties. Storage modulus (E') and loss tangent (tan δ) were measured using dynamic mechanical analysis (DMA 7 Perkin Elmer) in the compression mode with stainless steel parallel plate probe (1 mm diameter), at 1 Hz, on small samples ($3 \times 3 \times 2$ mm^3) regularly taken from a polymer plate. Static and dynamic (80% of static force) forces were chosen according to crosslinking progress and physical properties of materials. For example, these forces were respectively 300 and 240 mN at the beginning of the reaction and 1000 and 800 mN for high crosslinked materials. Measurements were carried out in the range $-125°C$ to $50°C$, at a rate of $5°C$ min^{-1}. Standard calibration was performed with n-decane ($T_m = -50°C$) and indium ($T_m = 156.6°C$).

RESULTS AND DISCUSSION

Glass transition temperatures of high molar mass polybutadienes are known for a long time. Thus, the values of pure cis-1,4- and trans-1,4-polybutadienes are very close in the range -95 to $-107°C$[21-23]. For pure 1,2-polybutadiene, higher values were observed depending on the tacticity (e.g. $-28°C$ for syndiotactic; $-4°C$ for atactic)[24]. In the case of low molar mass polybutadienes or 'liquid polybutadienes', in particular HTPBs, the glass transition temperatures are directly connected to their microstructure. For example, a value of $-75°C$ was reported in the literature[25] for the Poly Bd R 45 HT® which consists of 22% of 1,2 units and 78% of 1,4 units (23.7% cis and 54.3% trans)[26,27]. For an another oligomer of opposite microstructure, the Nisso G 2000® (88% of 1,2 units and 12% of 1,4 units), a higher value is measured ($-19°C$) in agreement with the general trend mentioned above for high molar mass polybutadiene[28]. It is noteworthy that the later values were obtained by using d.s.c. and that no mechanical measurements was attempted on these HTPBs. As a matter of fact, measurement is very delicate because of a liquid–liquid transition ($T_{l,l}$) at low temperature which disturbs the results. Nevertheless, we have considered that mechanical measurements had become

a necessity seeing that mechanical properties reported on HTPB, more or less crosslinked by diisocyanates, show an asymmetrical tan δ peak with a shoulder, at higher temperature, likewise more or less important. Generally, the extent of this additional peak strongly decreases when crosslinking increases. Up to now, no interpretation was given for this peak.

First and foremost, we studied mechanical properties of our initial liquid HTPB, before crosslinking, by using d.m.a. measurements. For this purpose, we were obliged to use a parallel plate probe of 10 mm diameter. Indeed, it is necessary to apply dynamic and static forces sufficiently high in the glassy state and sufficiently weak in the liquid state so that measurement can be possible. The compromise is very difficult to find, and many experiments were carried out in order to obtain acceptable results. This difficulty is probably the reason why no d.m.a. measurements are described in the literature. Storage modulus and tan δ are reported in *Figure 1*.

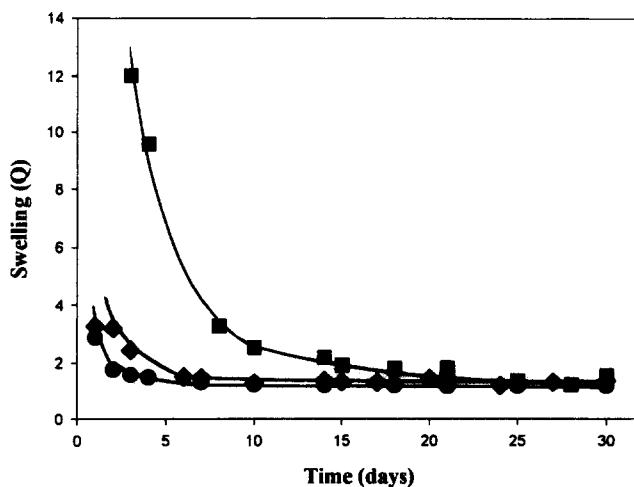Two mechanical transitions can be observed. The first

Figure 2 Swelling of PBU2Si in toluene versus crosslinking time at 80°C under moisture for [DBTL]/[Si] $= 0$ (■); 2×10^{-3} (♦); 5×10^{-3} (●)
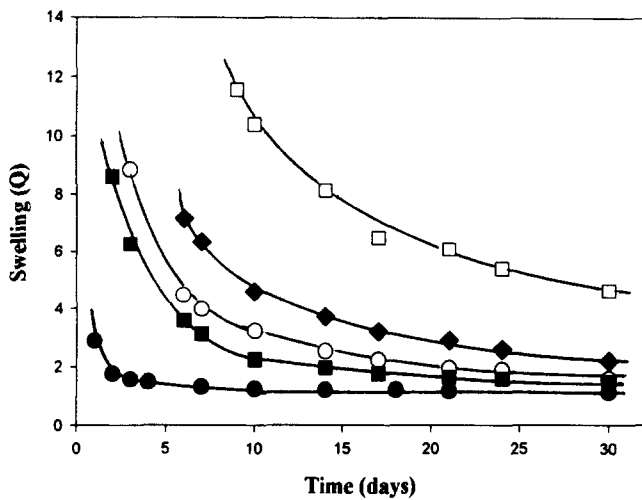
Figure 3 Swelling of PBU2Si in toluene versus time at different crosslinking temperatures: (□) room temperature; (♦) 40°C; (○) 60°C; (■) 80°C; (•) 80°C under moisture
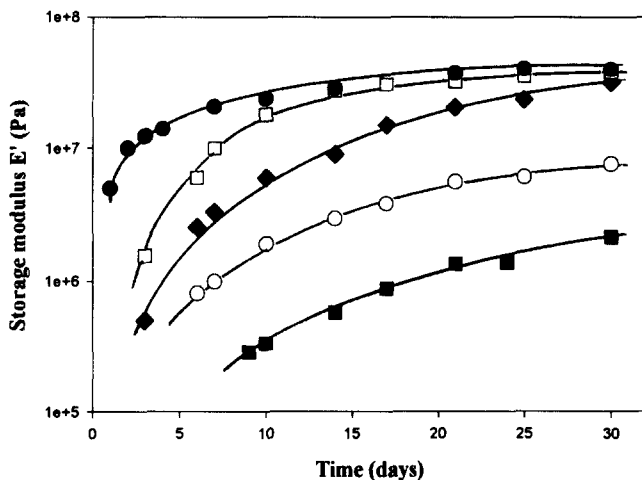

Figure 4 Storage modulus at the rubbery plateau (E') of PBU2Si versus time at different crosslinking temperatures: (■) room temperature; (○) 40°C; (♦) 60°C; (□) 80°C; (•) 80°C under moisture
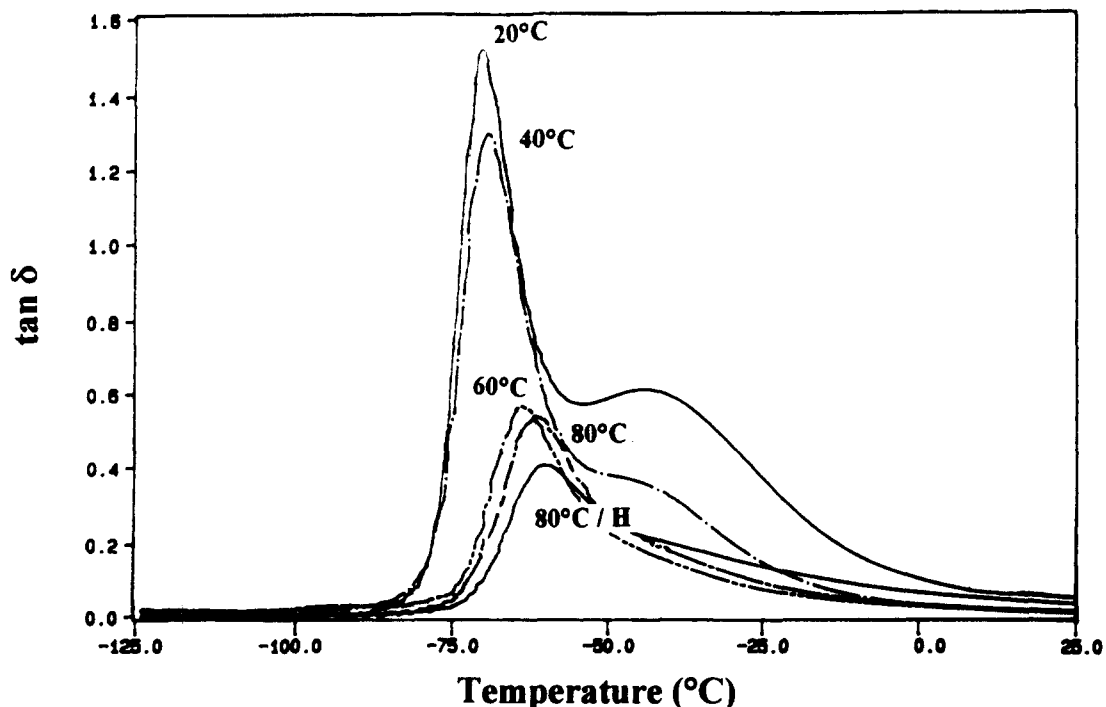
one ($-78°C$ at the onset of the E' curve or $-73°C$ at the apex of the tan δ curve) is connected to T_g in our experimental conditions. This is the only transition mentioned in the literature, and is assigned to mainly 1,4 repeating units[25]. The second transition (T_2) is clearly shown by a well-marked tan δ peak at $-55°C$ and is not observed by d.s.c. Nevertheless, this transition corresponds to a very weak variation of E' immediately followed by a modulus drop due to the liquid–liquid transition. It is the proximity of T_2 and $T_{1,1}$ which makes the observation very difficult. This transition was observed for different modified HTPBs, and by the way, a thorough study on the shifting of T_2 during crosslinking will be reported soon and will strengthen our present interpretation[29]. For the moment, our assumption is to assign T_2 to a mechanical transition of short vinyl sequences. This theory takes one's stand on structure considerations. The first one is that, on average, there is 11.5 vinyl units per chain with a mean length of vinyl sequences of 2.2 units according to Pham[30]. Therefore, vinyl diads to vinyl pentads, and even higher, may exist in the polymer chain. This remark can explain that HTPB exhibits two mechanical transitions, namely the glass transition, corresponding to the long 1,4 sequences, and an intermediate transition (T_2) as it was reported for tapered block copolymers of A–B type where three transitions (T_{gA}, T_{gA-B} and T_{gB}) are observed and where the intermediate one can be the chief transition [31,32]. In our case, we think that the weak variation of E' and the lack of signal by d.s.c. for the transition T_2 come from the low number of vinyl sequences in polymer chain.

Subsequently, we studied the crosslinking of polybutadienes bearing ethoxy silane groups. Networks are obtained by an initial hydrolysis of ethoxy silane followed by condensation of resulting silanol. Thus, these reactions, and consequently the ultimate properties of materials, depend on many parameters such as nature of catalyst, concentration of catalyst, the temperature, the moisture content, the reaction time, the number of silane functions per chain and the sample thickness.
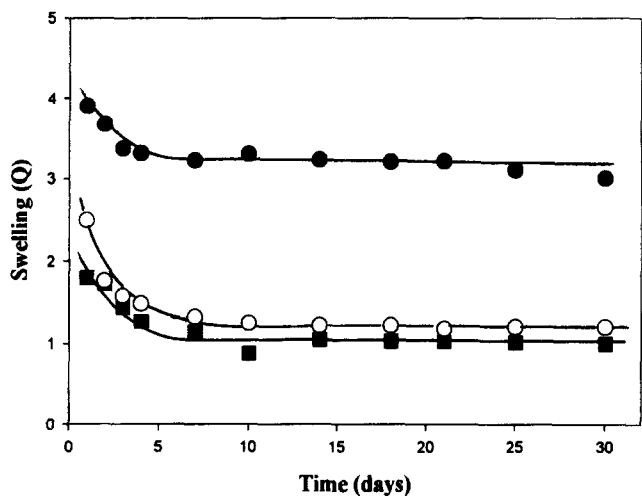

Figure 5 Tan δ versus temperature for PBU2Si after 30 days of crosslinking at different temperatures (20°C, 40°C, 60°C, 80°C and 80°C/humidity)

Figure 6 Swelling in toluene of PBUnSi versus crosslinking time at 80°C under moisture with [DBTL]/[Si] = 5 × 10^{-3} for n = 1.2 (•); 2 (●); 2.4 (■)

In the following section, we report the influence of catalyst and temperature only on PBU2Si and the effect of functionality for PBU1.2Si, PBU2Si and PBU2.4Si.

Influence of catalyst

Formation of a urethane bond often requires the use of catalyst and in our case, HTPB modifications were carried out in the presence of DBTL[20] ([DBTL] = 11.8 × 10^{-4} mol kg^{-1}; [DBTL]/[Si] = 2 × 10^{-3}). Thus, to measure the effect of catalyst on hydrolysis, we also synthesised a PBU2Si without catalyst (3 days instead of 1 h 30 min with DBTL). A third sample was prepared by adding a small amount of DBTL at the end of the synthesis in order to obtain [DBTL]/[Si] = 5 × 10^{-3}. An increase of viscosity and the formation of a skin at the surface was observed after about 6 days for catalysed samples, but these phenomena appear only after 2 weeks for the uncatalysed one. This preliminary result shows that in spite of the hydrophobic character of polybutadiene, hydrolysis occurs even at room
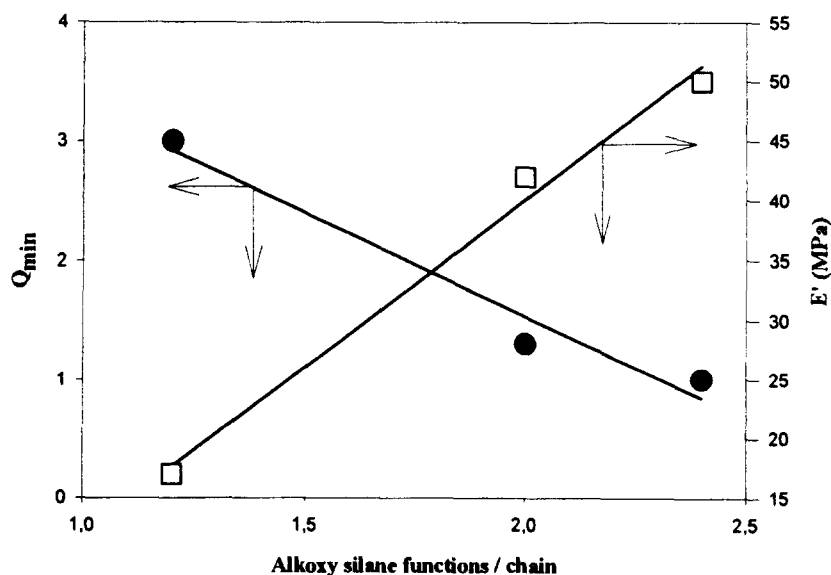

Figure 7 Limiting values of swelling (Q_{min}; ●) and storage modulus at the rubbery plateau (E'; □) versus n (ethoxy silane groups per chain)
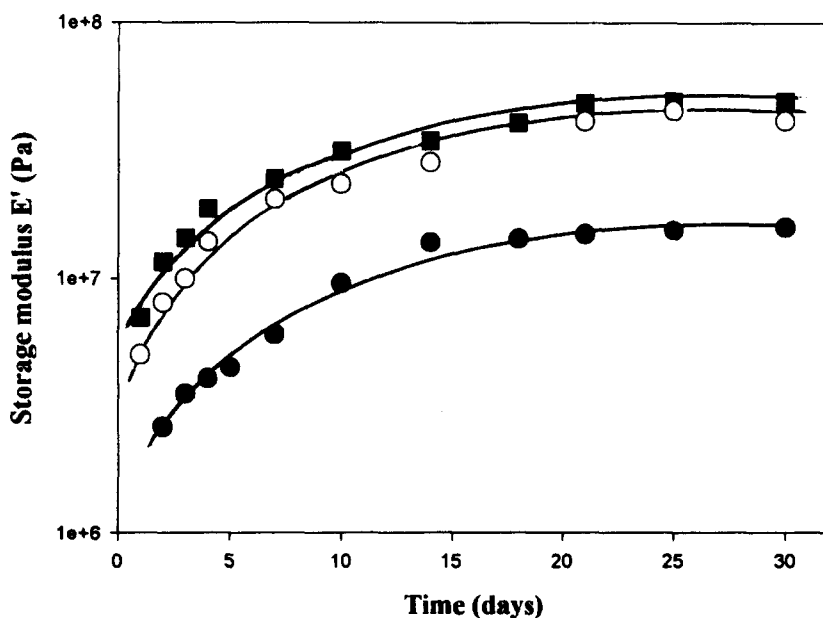

Figure 8 Storage modulus at the rubbery plateau (E') of PBUnSi versus crosslinking time at 80°C under moisture with [DBTL]/[Si] = 5 × 10^{-3} for n = 1.2 (●); 2 (○); 2.4 (■)
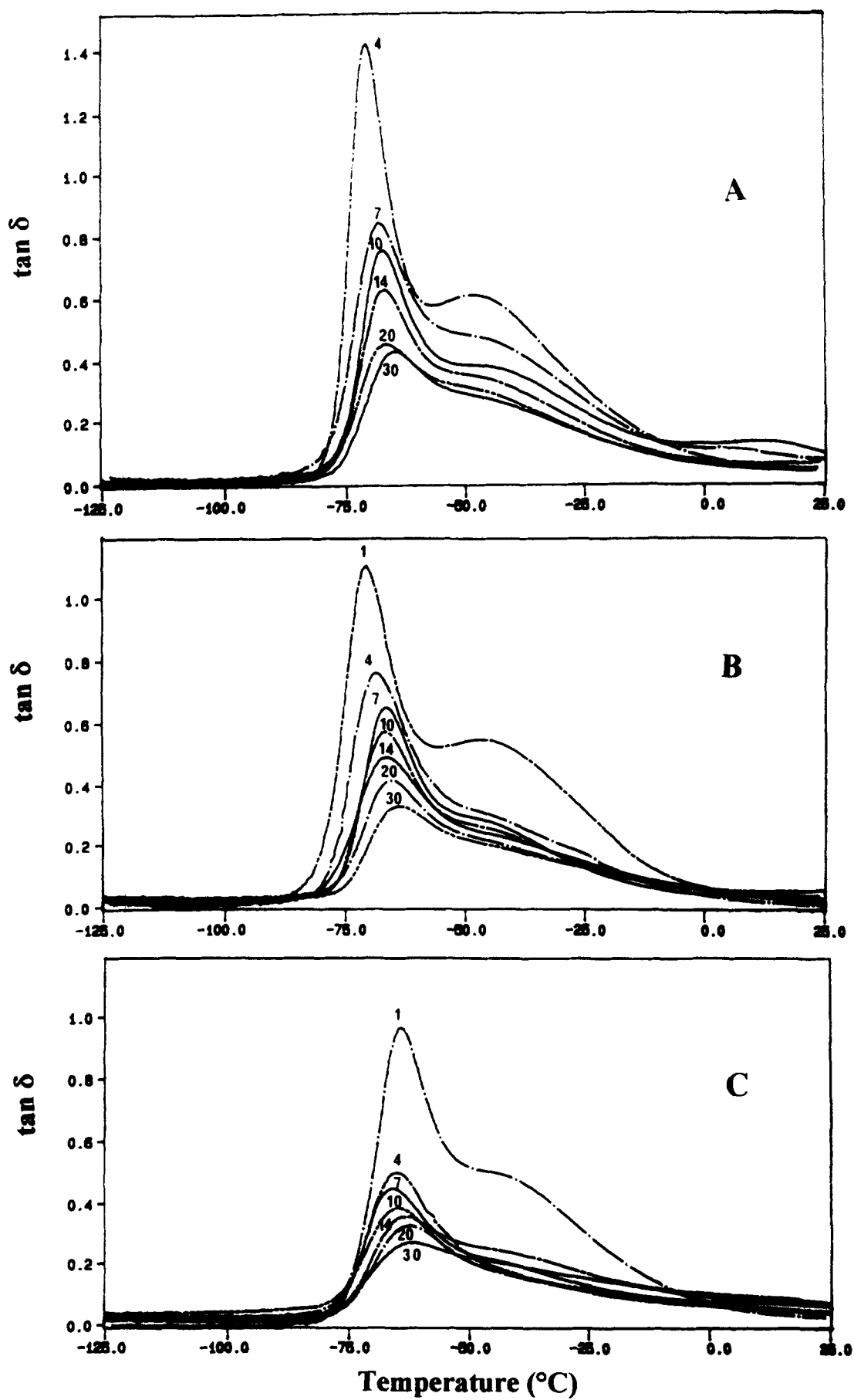
Figure 9 Evolution of tan δ versus temperature according to crosslinking time (days) for different values of *n*: 1.2 (a); 2 (b) and 2.4 (c)
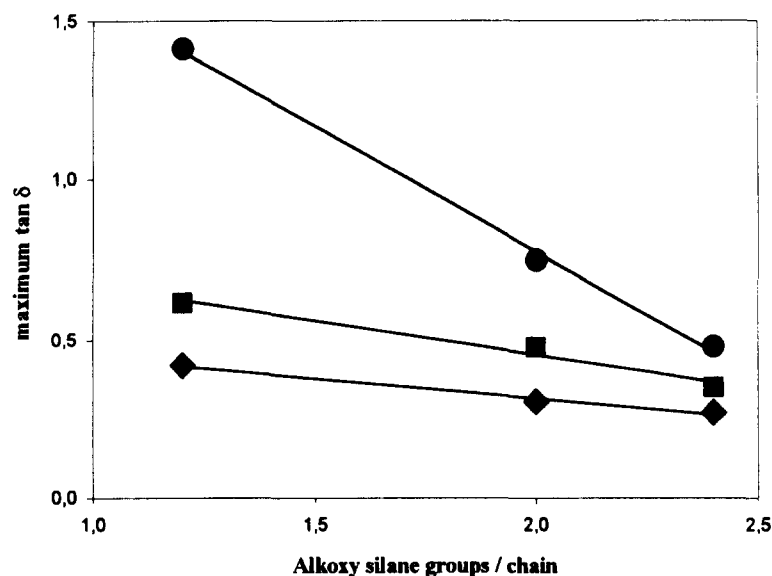
Figure 10 Variation of maximum intensity of tan δ peak versus number of ethoxy silane groups per chain (n) after 4 ($\bullet$); 14 ($\blacksquare$) and 30 ($\blacklozenge$) days of crosslinking at 80°C under moisture with [DBTL]/[Si] = 5 × 10^{-3}

temperature and implies it is imperative to protect catalysed compounds in hermetically sealed containers at low temperatures.

At 80°C and under moisture, crosslinking was considerably accelerated and swelling decreased rapidly (*Figure 2*). One can consider that the reaction was complete after 3–5 days with DBTL, depending on its concentration, and after 25 days without catalyst.

Influence of temperature

Swelling and mechanical properties were measured for PBU2Si with catalyst in the ratio [DBTL]/[Si] = 5 × 10^{-3} (*Figures 3–5*).

Swelling evolution (Q) and storage modulus (E') at the rubbery plateau measured at room temperature *versus* hydrolysis temperature show that the curves seem to tend to the same limiting values (Q_{min}~1.3 and $E_{max}' = 4.2 \times 10^7$ Pa) with rates increasing significantly with increasing temperature and with moisture (at 80°C). At room temperature and at 40°C, no measurement could be taken before 9 and 6 days respectively because the material was too soft and sticky. At these temperatures, crosslinking is not complete after 30 days and the polymer is colourless. In contrast, since 60°C, a fast increase of E' and a decrease of Q is observed. At 80°C, a plateau is rapidly reached with a marked colouration after 7 days and a hard skin is progressively formed.

In *Figure 5*, one can notice a very low shift of tan δ peak to higher T_g values with an important decrease of intensity. This drop of damping efficiency is also observed for the second transition T_2 and is characteristic of crosslinking progress. The very low increase of T_g may be explained by the low silane functionality which preserves almost entirely initial chain length even after crosslinking ($\overline{Mc} \approx \overline{Mn}$).

Influence of functionality

PBU1.2Si, PBU2Si and PBU2.4Si were studied for 30 days at 80°C, under moisture and in the presence of a catalyst ([DBTL]/[Si] = 5 × 10^{-3}). Whatever the functionality, a swelling plateau is reached for about 5 days (*Figure 6*). The different limits are nearly proportional to functionality (*Figure 7*) with $Q_{min} = 1$, 1.3, 3

respectively for $n = 1.2$, 2, 2.4 alkoxy silane groups per chain.

A similar result was obtained for E' at the rubbery plateau after 30 days (*Figure 7*) where $E' = 17$, 42, 50 MPa respectively for $n = 1.2, 2, 2.4$. Nevertheless, an increase in storage modulus was observed until 20 days (*Figure 8*) whereas swelling was already stabilised by that time.

In *Figure 9* are reported the different tan δ plots for each n value during 30 days. We can notice that the maximum of tan δ peaks do not considerably shift during crosslinking whatever the transition (T_g or T_2) and the n value, which can be due to molar mass per crosslinked unit ($\overline{Mc}$), is materially constant. However, a drop of damping efficiency is naturally obtained with crosslinking and a linear decrease is observed according to n values (*Figure 10*). Finally, the peak broadening is constant showing the same relaxation time distribution.

CONCLUSION

This study clearly shows that Q, E' and tan δ measurements allows us to perfectly follow crosslinking of polybutadiene bearing alkoxy silane functions (PBUnSi), where n is the number of silane groups per chain. According to n values, we are able to modulate swelling and mechanical properties whereas the glass transition temperature remains constant. It is now interesting to compare these results with a future report on immobilisation of alkoxy silane groups onto double bond which leads to a very different mechanical behaviour for the same values of n, while crosslinking occurs.

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